

General Meeting
of the
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Institute

**Astrobiology Space Missions:
What Will We Find on Mars,
Europa...?**

Exploring for Martian Life: Recent Results and Future Opportunities

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Introduction

The exploration for past or present Martian life and/or prebiotic chemistry are primary goals of the Mars exploration program. In implementing these goals, the Astrobiology community has consistently recommended an approach that will create the proper environmental context for exploration through the synergistic use of orbital reconnaissance and landed *in situ* science. These broadly-based investigations are regarded to be an essential prelude to the targeting of sites for *in situ* life detection experiments and sample return(s).

In exploring for Martian life, two independent investigation pathways have been identified by the Astrobiology community as co-priorities for missions preceding the 2007 opportunity. These include: 1) determining the locations of sedimentary deposits formed by past surface and subsurface hydrological processes (this will enable the exploration for a record of past life) and 2) mapping the three-dimensional distribution of water in all its forms (as a prelude to exploring potential habitats of subsurface liquid water that could sustain extant life).

The mantra, "follow the water", has been a guiding theme in constructing the new Mars exploration program architecture. It appears that over the next few opportunities (through 2007) implementation of this goal will be achieved through a combination of orbital mapping (infrared spectral mapping of mineralogy to identify ancient surface and subsurface water systems and radar sounding from orbit to locate reservoirs of modern subsurface water) and landed rover missions. Orbital missions in 2001 and 2005 will be interleaved with surface investigations in 2003 that will place twin "Mars Exploration Rovers" (MER A and B) at two high priority sites to gather information about surface mineralogy and petrology. This data will provide the basis for assessing the nature of ancient depositional environments at each site, while providing ground truth mineralogy that will assist in the interpretation of previously acquired orbital data.

Results from Mars Global Surveyor

The Mars Global Surveyor (MGS) orbiter, presently mapping at Mars, has produced a variety of new data that is being used to plan future missions. The Mars Orbiter Camera (MOC) experiment continues to provide high resolution images of the surface at many targeted locations on Mars. These data have: 1) confirmed the role of running water in the formation of many small valley networks in the ancient southern highlands of Mars, 2) revealed that volcanism was more widespread and continuous than previously thought, 3) shown that recently active surface seeps have carved channels on steep, poleward-facing

slopes at high latitudes and 4) that finely layered sediments of potentially aqueous origin are exposed on the floors of many craters and chasmata. Although the distribution of MOC coverage is presently quite spotty, at the highest (1.5 m/pixel) resolution, these data contributed importantly to the assessment of landing site safety for the 2003 landed mission. However, at the highest spatial resolution, surface features and processes have proven quite difficult to interpret. Mission planners have been forced to take a conservative approach in landing site certification. Overall, this had a negative impact on site selection for Astrobiology in limiting access to many high priority Astrobiology sites.

The Mars Laser Altimeter experiment (MOLA) has been a remarkably useful instrument, providing the first high resolution topographic maps of the Martian surface. Although still debated, MOLA data were used to test the hypothesis of a former ocean on the northern plains of Mars. MOLA has shown the northern plains to be the flattest surface in the Solar System, providing support for the suggestion of extensive near surface ice deposits at high latitude sites.

The Thermal Emission Spectrometer (TES) experiment, is mapping the Martian surface in the mid-infrared (5-12 μm), at a spatial resolution of ~ 3 km/pixel. This effort has produced the first regional scale compositional maps of the Martian surface which show fundamental compositional difference between the highlands (underlain by basaltic rocks) and the northern plains (which have a composition closer to basaltic-andesite). Spectral analysis of the TES data are being used to test the hypothesis that a previously dense atmosphere of carbon dioxide was sequestered in the Martian crust as carbonates. The absence of these mineral signatures in surface materials suggests that large limestone deposits are probably not exposed at the surface, although carbonates could be present in abundances below the detection limits of TES ($\sim 15\%$ by volume).

Although TES has yet to discover carbonates, it has detected large surface deposits of specular hematite at two sites (Terra Meridiani and Aram Chaos). In the former case, the coarsely-crystalline hematite appears to reside in an ancient paleolake basin, while in the latter case deposits occur in association with a large collapse (chaos) feature formed by outflows of subsurface water. The presence of specular hematite at these two sites suggests a prolonged period of hydrological activity, leading to aqueous alteration and/or chemical sedimentation. Finally, maps of thermal inertia obtained from TES data have provided important new information about rock abundances and grain size of surface materials needed for landing site safety certification.

NAI Mars Focus Group Activities

To provide a forum for engaging the broader Astrobiology community in scientific discussions about landing site priorities for the 2003 mission, the NASA Astrobiology Institute Mars Focus Group reviewed a number of high priority sites in two videocon meetings held in early January of this year. (Supporting information for this site review has is posted on the ASU Astrobiology website: <http://astrobiology.asu.edu/>). The content of these discussions, which were reported at the 2003 Landing Sites Workshop for MER A and B, held at NASA Ames on Jan. 24-25, 2001, will also be reviewed.

Europa: Views from the *Galileo* Mission

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Europa has the possibility of harboring a sub-surface liquid ocean, organic compounds, and a heat source from friction generated from tidal action. These potential conditions make Europa a high-priority for exobiological exploration. First viewed up-close during the *Voyager 1* and 2 flybys in 1979, the *Galileo* mission has provided a wealth of high-resolution data which have provided new insight into this Jovian satellite. Models for the interior derived from values of the moment of inertia suggest that Europa is a rocky object with a central core and an outer shell of water composition some 150 km thick, the surface of which is frozen. *Galileo* magnetometer data suggest that a sub-ice zone of salt water could exist, although this interpretation is model-dependent. Remote sensing data includes spectra from the *Near Infrared Mapping Spectrometer (NIMS)*, which show the presence of salts and sulfur compounds mixed with the ice, and images from the *Solid State Imaging (SSI)* system. From 23 near and distant flybys of Europa, more than 525 images were taken, with resolutions ranging from 11 m/pixel to 20 km/pixel.

Europa is seen to have a geologically young surface dominated by tectonic and possible cryovolcanic (*e.i.*, generation of “magmas” consisting of volatiles such as water) activity which form complex ridge sets, zones of ice-crust separation, and areas in which the crust is disrupted and reformed. These areas suggest that materials from beneath the ice crust have been emplaced on the surface and have NIMS signatures showing the presence of non-ice compositions. The few large impact structures on Europa show excavation of similar compositions from the subsurface. Non-ice materials are also inferred to be implanted on the surface from exogenic sources, such as the volcanically-active moon, Io.

Under the sponsorship of the *NASA Astrobiology Institute*, an informal *Europa Focus Group* was organized to provide a forum for discussion and to promote interdisciplinary research. The first workshop was held at NASA-Ames Research Center in February, 2001, during which key questions were posed for future work. These include:

- I. What is the surface composition of Europa, and is it possible to distinguish among endogenic, exogenic, and “weathering” components and sources?
- II. How do geological processes affect the physical and chemical properties of the surface and near-surface icy crust (drawing on knowledge of terrestrial ice, etc.)?
- III. Where are the sites/niches/environments favorable for exobiology in Europa (again drawing on terrestrial considerations, etc.)?

IV. Is potential recycling in the ice and/or liquid water of Europa steady or episodic, and what are the implications for exobiology?

V. What are the plausible models for the origin and evolution of life on Europa?

VI. What are the potential signatures of life on Europa, and do they exist?

Future *Europa Focus Group* workshops will be organized to assess the current state of knowledge on these and other issues, such as future exploration of Europa by spacecraft.

The Source of Extraterrestrial Water in Martian Meteorites

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Introduction: Polycyclic aromatic hydrocarbons were reported in Martian meteorite ALH 84001, and were interpreted as one of several lines of evidence for ancient life on Mars (1). For life to exist on any planet, water must be present. Geomorphological features on the surface of Mars suggest that water was abundant in its early history (2, 3, 4). Hydrogen isotopes measured on Martian meteorites provide important clues on the history and source of water on Mars. The Martian atmosphere is 5.2 times enriched in D/H relative to terrestrial values. Interaction of Martian meteorites with a water reservoir that equilibrated with the Martian atmosphere was invoked to explain the D enrichment in minerals from Martian meteorites (5). So, in principle the H isotope signatures of Martian meteorites of different ages may provide clues on the H isotope compositions of the water reservoirs on Mars and on the evolution of the Martian atmosphere through time. Recently (6, 7, 8) reported D enrichment in impact glasses and in post-stishovite high pressure polymorph of silica in Martian meteorites. This finding calls for a reassessment of the role of shock metamorphism in hydrogen isotope fractionation.

Techniques: The petrography, shock history, and H isotope composition of the water-bearing phases in Martian meteorites ALH 84001, EETA 79001, ALHA 77005, QUE 94201, Chassigny, Zagami, and Shergotty were investigated. The ion probe analyses were performed with a 12.5 Kv Cs⁺ beam of ~ 2 nA, 5 Kv secondary accelerating voltage and an electron flood gun for charge compensation. The analyzed areas ranged from 5-25 μm . When necessary, the hydrogen blank contribution was measured on olivine and subtracted from the analyses. Three rhyolite glasses (0.297 to 0.992 wt. % water) and an amphibole (2.03 wt. % water) were used as standards for both H isotope and water abundance measurements.

Results: The water-bearing phases show evidence of a deuterated extraterrestrial component mixed with a terrestrial H contaminant. All the studied meteorites with the exception of Chassigny contained impact melted feldspathic glasses that show a wide range in their δD values even within the same meteorite. The lowest δD value for feldspathic glass (314‰) was observed in QUE 94201 and the highest (2760‰) in

ALHA 77005. Mafic glass produced by localized impact melting was only observed in ALHA 77005 and EETA 79001, and it tends to have higher δD values (1301 to 3031‰) than the feldspathic glass. Shocked plagioclase in Chassigny (unmelted) has lower δD values (90 to 688‰) relative to the impact melted feldspathic glass. The highest δD values measured were for the post-stishovite silica in Zagami (1960 to 3728‰).

Discussion: In principle, it can be argued that the D enrichment in the impact glasses and post-stishovite silica was acquired by equilibration of these phases with a crustal water reservoir on Mars that equilibrated with the Martian atmosphere. These phases, however, formed by shock metamorphic processes at pressures of ~35 to 80 GPa. This suggests that impact metamorphism may have contributed to the H isotope fractionation observed in the impact glasses and post-stishovite silica. Shock experiments (9) showed significant loss of water by impact, and the remaining water in the shocked targets became isotopically heavy. The magnitude of fractionation increases with pressure and with the degree of melting in the samples. At low pressure (<10 GPa, $T \leq 1500K$), the species lost was molecular water, while at higher shock pressures (20-30 GPa, $T \sim 1500-2000K$), H_2 became the predominant species. Extrapolation of these data to the pressure range of impact metamorphism in the studied meteorites (35-80 GPa) suggests that atomic H may become dominant. The isotopic fractionation as a function of hydrogen loss is greatest when atomic hydrogen dominates. It is, therefore, likely that surface water or a less fractionated fossil underground water was dissolved at high pressure in the impact melts and further H isotope fractionation occurred due to H loss by devolatilization. The δD values of the magmatic glass in melt inclusions reported by (6, 10) are significantly lower (-18 to +304‰) than the δD values of impact glasses and post-stishovite silica. They may represent the closest approximation of a magmatic signature on Mars. Any magmatic H signature in the precursors of the impact glasses however, was modified or erased during the impact process.

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Radiolytic Chemistry at Europa's Doorstep – The First Meter

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Galileo Orbiter observations have revealed a relatively young ($10^7 - 10^8$ year old) icy surface with a molecular composition in the sensible top millimeter layer largely driven by radiolytic energy inputs and sputtering from magnetospheric particle irradiation. The observed sulfate hydrates (e.g., MgSO_4 or H_2SO_4), surface (H_2O_2) and atmospheric (O_2 , O) oxidants, and sodium neutral cloud are characteristic of a heavily irradiated ice surface with access to endogenic and exogenic sources of sulfur and other non-ice materials. Leading/trailing asymmetries suggest magnetospheric plasma and energy inputs, while concentrations along tidal cracks are more indicative of salt water evaporites from the putative sub-surface ocean. Sputtering by magnetospheric ions produces vertical escape to space of lighter chemical species such as hydrogen and sodium. The ease of hydrogen escape from the irradiated surface and atmosphere allows buildup of oxidants on the surface. Horizontal dispersion of endogenic sulfur by sputtering on the trailing hemisphere, and larger energy inputs there from magnetospheric irradiation, could account for higher abundance of sulfates in that hemisphere. Although the magnetospheric particles irradiate the ice mainly at depths of microns to millimeters, the residual irradiation products can be buried to meter depths in the ice regolith by meteoritic gardening over the apparent surface lifetime of millions of years. Large reservoirs of such products may reside below the visible surface and eventually be transported to the sub-surface ocean as the result of crustal instabilities driven by tidal forces and thermal gradients. Measurements of vertical profiles for irradiation products could be a prime focus for meter-depth probe experiments on a Europa lander spacecraft.

Cooper *et al.* (2001) have reported, as upper limits derived from the incident energy fluxes of magnetospheric particles, that the radiolytic production rates of H_2O_2 and O_2 are sufficient to fully saturate the 100-km deep ocean with dissolved oxygen in 10^7 years. Since reduced gases may be released from the ocean bottom at hydrothermal vents, the chemical disequilibrium required for evolution of life within Europa may present even without substantial inputs from photosynthetically active radiation (PAR) at the surface. Europa may therefore represent a new class of habitable objects in the universe – large icy satellites or planets orbiting in intense irradiation environments. Due to the fragility of life often exposed to catastrophic events on the surfaces of planets in the classical ‘habitable zone’, life forms evolving in protected sub-surface oceans of Europa-like objects might actually be more common in the universe than terrestrial life forms. Interplanetary transfer of astrobiological material in escaping ejecta from cometary impacts on such objects could then continually reseed terrestrial environments.

Cooper, J. F., R. E. Johnson, B. H. Mauk, H. B. Garrett, and N. Gehrels, Energetic Ion and Electron Irradiation of the Icy Galilean Satellites, *Icarus*, **149**, 133-159, 2001.

Beagle 2: The Next Exobiology Mission to Mars

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Beagle 2 is a 60 kg probe (with a 30 kg lander) developed in the United Kingdom for inclusion on the European Space Agency's 2003 Mars Express. Beagle 2 will deliver to the Martian surface a payload which consists of a high percentage of science instruments to landed spacecraft mass. Beagle 2 will be launched in June, 2003 with Mars Express on a Soyuz-Fregat rocket from the Baikonur Cosmodrome in Kazakhstan. Beagle 2 will land on Mars on December 26, 2003 in the Isidis Planitia basin (~10°N and 275°W), a large sedimentary basin that overlies the boundary between ancient highlands and northern plains. Isidis Planitia, the third largest basin on Mars, which is possibly filled with sediment deposited at the bottom of long-standing lakes or seas, offers an ideal environment for preserving traces of life.

Beagle 2 was developed to search for organic material and other volatiles on and below the surface of Mars in addition to the study of the inorganic chemistry and mineralogy [1]. Beagle 2 will utilize a mechanical mole and grinder to obtain samples from below the surface, under rocks and inside rocks. A pair of stereo cameras will image the landing site along with a microscope for examination of surface and rock samples. Analyses will include both rock and soil samples at various wavelengths, X-ray spectrometer and Mossbauer spectrometer as well as a search for organics and other light element species (e.g. carbonates and water) and measurement of their isotopic compositions. Beagle 2 has as its focus the goal of establishing whether evidence for life existed in the past on Mars at the Isidis Planitia site or at least establishing if the conditions were ever suitable. Carbonates and organic components were first recognized as existing on Mars when they were found in the Martian meteorite Nakhla [2,3]. Romanek et al. [4] showed the carbonates in ALH84001 were formed at low temperatures. McKay et al. [5] noted possible evidence of early life on Mars within the

ALH84001 meteorite. Thomas-Keptra et al. [6] showed the magnetite biomarkers in ALH84001's carbonates are indistinguishable from those formed by magnetotactic bacteria found on Earth. Gibson et al. [7] showed there was significant evidence for liquid water and biogenic products present on Mars across a 3.9 billion year period.

A mechanical arm (PAW) operates from the lander and is used for science operations along with sample acquisition. Instruments attached to the PAW include: stereo cameras, Mossbauer instrument, X-ray fluorescence instrument, microscope, environmental sensors, rock corer/grinder, a spoon, mirror, brushes, a mole attachment for acquisition of subsurface to depths of 1 to 2 meters and an illumination device. Each camera has 14 filters which have been optimized for mineralogy composition, dust and water vapor detection. The microscope's camera is designed for viewing the size and shape of dust particles, rock surfaces, microfossils, and characteristics of the samples prior to introduction into the gas analysis package (GAP). The camera has a resolution of 4 microns/pixel, features 4 color capability (red, green, blue and UV fluorescence), a depth of focus of 40 micrometers and translation stage of ± 3 millimeters.

The heart of the Beagle 2's life detection package is the gas analysis package (GAP) which consists of a mass spectrometer with collectors at fixed masses for precise isotopic ratio measurements and voltage scanning for spectral analysis. Primary aim of the GAP is to search for the presence of bulk constituents, individual species, and isotopic fractionations for both extinct and extant life along with studying the low-temperature geochemistry of the hydrogen, carbon, nitrogen and oxygen components on Mars from both the surface and atmosphere. GAP is a magnetic sector mass spectrometer with the range of 1 to 140 amu which can be operated in both the static and dynamic modes. A triple Faraday collector array will be used for C, N and O ratios along with a double Faraday array for H/D. Pulse counting electron multiplier will be utilized for noble gases and selected organics. Anticipated detection limits are at the picomole level for operation in the static mode of operation and high precision isotopic measurements will be made in the dynamic mode. Sample processing and preparation system consists of reaction vessels along with references. Sample ovens capable of being heated are attached to the manifold for sample combustion. Surface, subsurface materials and interior rock specimens will be combusted in pure oxygen gas at various temperature intervals to release organic matter and volatiles. Combustion process will permit detection of all forms and all atoms of carbon present in the samples. A chemical processing system is capable of a variety of conversion reactions. Gases are manipulated either by cryogenic or chemical reactions and passed through the gas handling portion of the vacuum system. There are two modes of operation: quantitative analysis and precise isotopic measurements.

Three main types of analysis will be carried out by the GAP: (1) search for organic matter, (2) stepped combustion for total light element content and speciation, and (3) atmospheric analysis. Isotopic measurement of H/D, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{17}\text{O}/^{16}\text{O}$, and $^{18}\text{O}/^{16}\text{O}$ and search for possible biogenic methane within the Martian atmosphere will be made. Estimates of the present methane concentration in the atmosphere is believed to be <100ppb. Lifetime of CH_4 in Mars' atmosphere is believed to be < 300 years and therefore no abiogenic methane is anticipated. The GAP is capable of concentrating

gases and the search for biogenic atmospheric methane will be made. The mass spectrometer will operate in the static mode for the CH₄ measurements after chemical reagents have concentrated the atmospheric gases. Conversion to a measureable component will be carried out to ensure no false positive results will be obtained along with lowering the detection limits for methane. Should methane be detected within the Martian atmosphere its putative source would have to be biogenic (i.e. methanogenic bacteria).

An environmental sensor system for surface temperatures, atmospheric pressures, wind speed and direction is also to accompany atmospheric sampling. Particle radiation environment's dose and rates will be characterized. UV flux at the lander will be measured in a variety of wavelength bands longer than 200nm, information relevant to understanding the survival of organics. High sensitivity isotopic analysis of the carbon species present within the samples makes no assumptions about the biochemistry on Mars but provides clues to past life as inferred from the isotopic fractionations measured directly on Mars. Isotopic fractionation signatures from biogenic processes will survive even in altered rocks. Planetary protection protocols will be followed for Beagle 2. The lander has been designated as a Category IVA⁺ mission. A microbial reduction plan is in place and all components will be sterilized. Additional cleaning procedures will be followed to reduce blanks associated with GAP operations.

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Europa: Crunchy or Chewy Inside?

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The presence of molten rock within a few kilometers of the water-rock inter-face in Europa is far more important for life than the presence of a liquid ocean. Hydrothermal vent communities on Earth depend on a flux of melt from the mantle into the lithosphere to drive the high-temperature chemistry that liberates nutrients from the rock. Europa's major internal energy sources at the present time are radioactive decay and tidal heating. In a body smaller than the Moon, consisting partly of ice and having a significant iron core, radiogenic heat production is quite small, probably not exceeding a few times 10^{11} W. Tidal dissipation is capable of much greater heating rates and occurs both in the silicate and icy portions of the body. The maximum temperature reached within Europa's mantle depends on the balance between dissipation and heat transfer. Due to the sensitivity of both tidal heating and convective heat transfer on viscosity, there exist two stable equilibrium states for Europa's mantle: crunchy (Moon-like), in which weak subsolidus convection balances radiogenic heat production, and chewy (Io-like), in which the mantle is extensively molten and undergoes vigorous convection. Understanding the current state of Europa's interior is critical to assessing the potential for life.

The current state of Europa's interior, though not accessible to our cameras or the limited geophysical observations of Galileo, may be probed by investigating its affect on the evolution of Europa's orbit. Tidal dissipation in a chewy Europa drives the evolution of its orbit more rapidly than the crunchy Europa would. The question can then be asked: if Europa is highly dissipative, what are the chances that we are observing it in its current orbital state? Europa's present large eccentricity may not survive very long if a chewy center is dissipating Io-like amounts of energy. If the lifetime of the current eccentricity is found to be short (less than 10^5 years) then we may conclude that it is unlikely that we have stumbled upon Europa in a very special era of its history and that the interior is cold and crunchy: not the kind of place to look for life.

Magnetofossils in Terrestrial Samples and Martian Meteorite ALH84001

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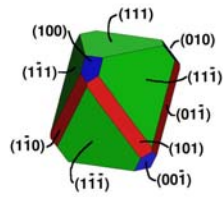
Introduction: Here we compare magnetite crystals produced by terrestrial magnetotactic bacteria strain MV-1 with a subpopulation of magnetites from ALH84001. We find both to be chemically and physically identical -- specifically, both are single-domain, chemically pure, and exhibit an unusual crystal habit we describe as truncated hexa-octahedral [1]. On Earth such truncated hexa-octahedral magnetites are only known to be produced by magnetotactic bacteria. We suggest that the observation of truncated hexa-octahedral magnetites in ALH84001 are both consistent with, and in the absence of terrestrial inorganic analogs, likely formed by biogenic processes.

Magnetotactic bacteria strain MV-1: Six specific properties of biogenic magnetite can be identified that when met collectively, constitute a rigorous biosignature (i.e., one that is not produced by natural inorganic processes) [2]. These are: (1) narrow size-range (i.e., single-domain for uniform magnetization) and shape (restricted width-to-length (W/L) ratios); (2) chemical purity; (3) few crystallographic defects; (4) truncated hexa-octahedral morphology (Fig 1.); (5) elongation along the [111] axis; and (6) alignment in chains within cells. These properties all act to optimize the interaction of the magnetites with a magnetic field. Since the strength of magnetic field interactions are much smaller than thermal energies kT , on thermodynamic grounds alone, chemical and biological processes cannot be influenced by magnetic fields to any measurable degree [3]. Hence the six characteristics, outlined above, have *evolved* through the process of natural selection. No published reports of inorganic truncated hexa-octahedral magnetites are known.

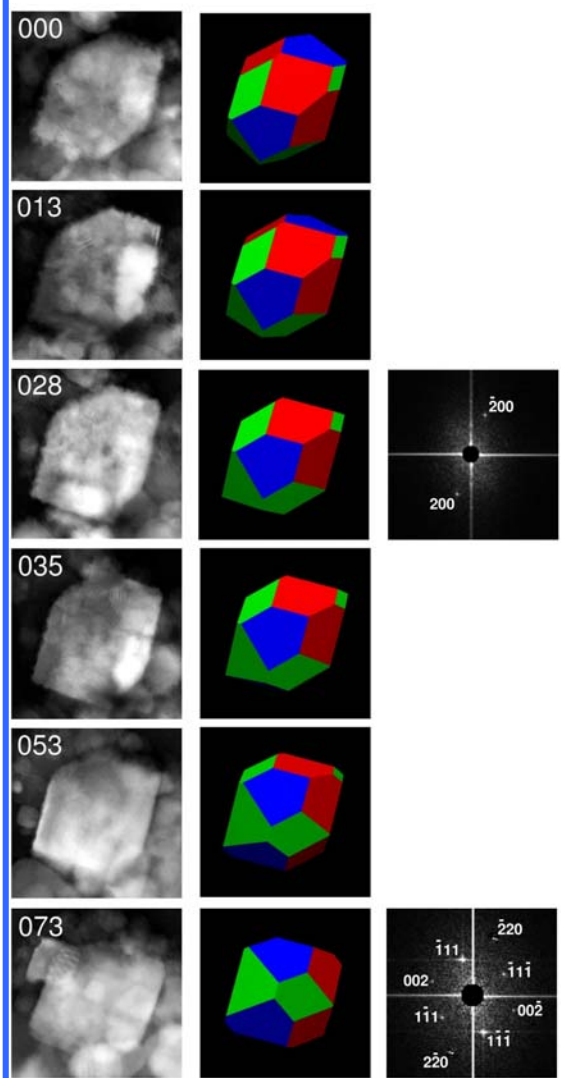
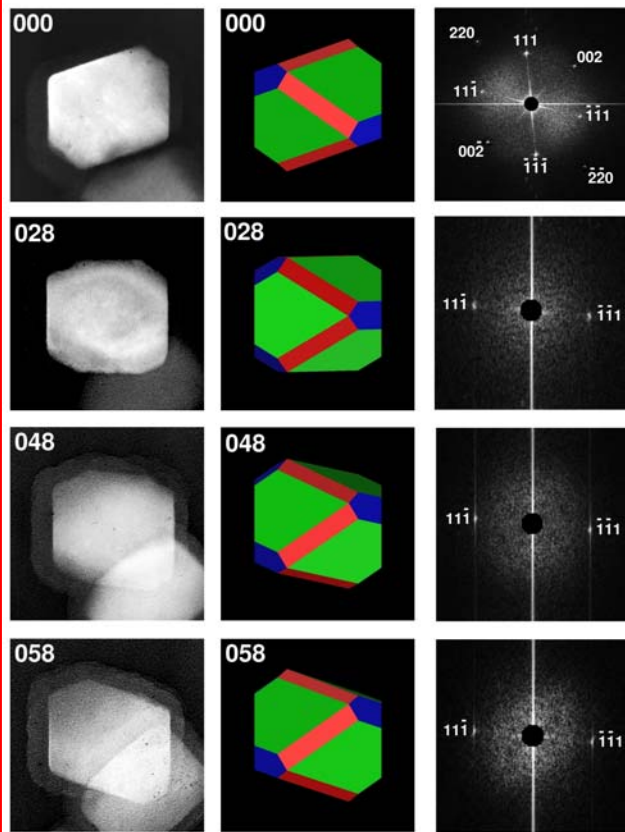
ALH84001 Truncated Hexa-octahedral Magnetites: Approximately 25% of the Martian magnetites, found embedded in ~3.91 Ga old carbonate globules [4], display 5 of the 6 properties described previously (since our extraction procedure destroyed spatial relationships, the presence aligned magnetite chains could not be evaluated). While the Martian truncated hexa-octahedral magnetite crystals are indistinguishable from those produced intracellularly by magnetotactic bacterium strain MV-1 [1,2] (Fig. 1), they are both chemically and physically distinct from the remaining ~75% of the magnetites in ALH84001. These other magnetites appear analogous to terrestrial inorganic magnetites (intimate mixtures of both biogenic and abiotic magnetite crystals [2] are observed in terrestrial samples of both recent and ancient carbonates).

Summary and Conclusions: Truncated hexa-octahedral magnetites on Earth are exclusively the product of biogenic activity -- no natural or synthetic inorganic process is known that could explain the observation of truncated hexa-octahedral magnetites in a terrestrial sample. Unless there is an unknown and unexplained inorganic process on Mars, which is conspicuously absent on the Earth, we suggest that ALH84001 truncated hexa-octahedral magnetites formed by a mechanism similar to its terrestrial biogenic counterpart. *As such, these crystals are interpreted as Martian magnetofossils and constitute evidence of the oldest life yet found.*

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**Truncated
Hexa-octahedron**



Astrobiology Investigations at a Martian Hematite Site

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Introduction: Christensen et al. (1), using data from the Mars Global Surveyor Thermal Emission Spectrometer (TES), have identified gray crystalline hematite in a 350 km by 750 km region near Sinus Meridiani. The deposit corresponds closely to the low-albedo highlands unit “sm”, mapped as a wind-eroded, ancient, subaqueous sedimentary deposit (2). Christensen et al. (3) interpreted the Sinus Meridiani deposit to be “an in-place, rock-stratigraphic sedimentary unit characterized by smooth, friable layers composed primarily of basaltic sediments with approximately 10 to 15% crystalline gray hematite.”

Christensen et al. (1) discussed five possible mechanisms for the formation of this deposit: direct precipitation from standing, oxygenated, Fe-rich water; precipitation from Fe-rich hydrothermal fluids; low-temperature dissolution and precipitation through mobile groundwater leaching; surface weathering and coatings; thermal oxidation of magnetite-rich lavas. Four of these mechanisms involve the interactions of rock with water, and thus have implications in the search for evidence of microbial life.

Direct precipitation from standing, oxygenated, Fe-rich water: Iron formations are “chemical sediments, typically thinly-bedded or laminated, whose principal chemical characteristic is an anomalously high content of iron, commonly but not necessarily containing layers of chert.” (4). Iron formations are among the most common chemical sedimentary deposits of the Precambrian. The iron occurs as oxides, principally hematite and magnetite.

Precipitation from Fe-rich hydrothermal fluids: Hematite is one of several iron minerals that can form when large volumes of hydrothermal fluids move through rocks. The mineralogy of a hydrothermal zone is typically complex, reflecting local changes in temperature, pH, fluid composition, and other variables (5). For example, detailed studies of two silica-depositing hot springs (48-55°C) determined that iron was partitioned among hematite, goethite, ferrihydrite, siderite, and the iron smectite nontronite (6).

Low-temperature dissolution and precipitation through mobile groundwater leaching: Iron-rich laterites and ferricretes are formed on Earth when acidic groundwaters extensively leach soil and rock. Mafic minerals are unstable in acidic reducing environments and form colloidal iron oxides and hydroxides. These can be transported by water and redeposited if Eh and pH rise (5).

Surface weathering and coatings: Rock varnish, a complex combination of clays with Fe- and Mn- oxides and hydroxides, coats the surfaces of exposed rocks in many arid environments (7). Hematite, maghemite, and magnetite have been identified in rock varnish (8). The coatings are derived from airborne dust and other sources external to the rock, apparently deposited in the presence of thin films of water (9).

Hematite Deposits and Microbial Life: Several of the mechanisms proposed for hematite formation include microbial mediation, and microorganisms are sometimes preserved in the terrestrial deposits.

Iron Formations: Many iron formations contain fossil evidence of microbial life. In fact, the very existence of terrestrial iron formations has been interpreted as evidence of photosynthesizing organisms which significantly increased the percentage of oxygen in Earth's atmosphere and oceans (10).

The 2.0 Ga Gunflint banded iron formation contains abundant filamentous and coccoidal microorganisms preserved in chert layers (11). Current studies of Gunflint samples are documenting the preservation of similar microfossils and biofilm by hematite in the alternating iron-rich layers (12).

Hydrothermal Systems: Iron oxides precipitate with silicon dioxide or calcium carbonate in many hydrothermal systems. Wade et al. (6) noted the remains of rod-shaped bacteria and dehydrated biofilm in a silica-dominated iron hot spring, along with hematite and other minerals.

The preservation of microfossils in hydrothermal deposits is strongly dependent on temperature and solution chemistry. In the silica-dominated iron hot spring studied by Wade et al. (6), bacteria and biofilm were poorly preserved. However, recognizable bacterial remains were reported in iron oxide and manganese oxide deposits within hot spring travertines (13).

Iron-Rich Laterite and Ferricrete Soils: Microbes are ubiquitous in terrestrial soils. Bioloads of 10^6 to 10^9 bacteria per gram are typical, with organic-rich surface soils generally containing more organisms than deeper mineral soils (14). Many microbes can derive energy from the reactions of iron and oxygen in soils. Specialized bacteria oxidize iron from Fe^{2+} to insoluble Fe^{3+} in acidic environments such as mine tailings.

The preservation of microorganisms in laterites and ferricretes is poorly documented. Wielinga et al. (15) characterized the microbiology of fluvially deposited sulfidic mine drainages that formed a ferricrete, but significantly more research is required in this area.

Rock Varnish: Natural rock varnish has been shown to be a product of microbial activity (16). Initial studies demonstrated the presence of bacteria known to cause precipitation of manganese oxides (17). Bacteria isolated from natural varnish samples and cultured produced varnish similar to natural material.

Bacteria grow on rock and varnish surfaces, eventually becoming incorporated in the varnish layers. Mineralization occurs at ambient temperatures, resulting in partial preservation of cellular material. Organics preserved in varnish from Australia have been radiometrically dated at 36,000 years (7).

Discussion: The hematite deposits at Sinus Meridiani and other locations are the only places on Mars at which a specific mineral has been identified and correlated with a mappable geologic unit. These deposits may be the only large-scale mineralogical evidence for water-rock interactions early in the planet's history.

On Earth, diverse microbiota have been identified in each of the four "wet" environments discussed by Christensen et al. (1) for hematite deposition. Microfossils are preserved by hematite and related iron oxides in the geologic record. They are preserved by hematite in Precambrian iron formations and by manganese and iron oxides in rock varnish and in some hydrothermal systems.

If the hematite deposits carry a record of martian life, it will probably not be revealed by spacecraft instruments. Fossil microorganisms are only detectable by optical microscopy of thin sections or by electron microscopy. Thus, confirmation of ancient martian life by direct fossil evidence will require the return of samples to terrestrial laboratories. A key function of the next generation of Mars landers may thus be to discover and certify prime sites for future Mars sample return missions. The hematite deposits may well be among those prime sites.

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Confirmation of Spectrally Interpreted Mineralogy of Badwater Basin, Death Valley, CA: Applications to Identification of Evaporite Minerals on the Martian Surface

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The exploration for past or present Martian life is a high priority goal of NASA's Mars Program [1]. The present plan is to identify sites of ancient aqueous sedimentary environments on Mars by orbital reconnaissance, then conduct in situ robotic exploration at key sites (e.g. those that show evidence of past or present liquid water). Surface exploration will eventually lead to targeted selection and return of samples to Earth. Sites of particular importance for Astrobiology include sites of hydrothermal mineralization and evaporite deposition, among others [2]. The Thermal Emission Spectrometer (TES), currently in orbit at Mars has so far only identified concentrations of specular hematite (an aqueous mineral) at a limited number of sites. This is perhaps not surprising, given the spatial resolution of TES (3km/pixel)[3]. This year the Mars Odyssey orbiter will deliver a much higher spatial resolution infrared instrument, the Thermal Emission Imaging Spectrometer (THEMIS), to Mars orbit which will map a substantial part of the Martian surface at a spatial resolution of 100m/pixel. This should greatly improve our ability to find aqueous minerals that may be present at abundances below the detection limits of TES.

The Badwater Basin of Death Valley, CA provides an excellent analogue for evaporite basins that may have existed on Mars earlier in the planet's history. Moersch and Farmer [3] recently conducted a study of evaporite deposits in the Badwater Basin using MODIS/ASTER (MASTER) Airborne Simulator data. MASTER contains 50 channels (spectral bands), 10 of which fall within overlap the range of THEMIS. To simulate the data from TES and THEMIS, Death Valley MASTER data was de-resolved to match the respective spatial resolutions of those two instruments. The spectra were then cross-referenced to Arizona State University's TES library [4] and analyzed for evaporite spectral signatures. At TES spatial resolution, ENVI (remote sensing analytical, software

tool) identified only a few of the minerals detected at full resolution. However, when the data was de-resolved to simulate THEMIS resolution, evaporites were easily detected.

To evaluate the validity of the spectral mapping by Moersch and Farmer [3], we have conducted detailed field and laboratory analyses of surface samples collected from 16 sites in the Badwater Basin during May and October 2000. Sites were selected to cover the range of spectral end-members identified by Moersch and Farmer [3]. The surface morphology of each site was photo documented and surface samples collected, taking care to avoid mixing with subsurface materials. In the lab, samples were thin sectioned for petrographic analysis and analyzed by X-ray diffraction. In addition, thermal emission lab spectra were also acquired using a laboratory version of the TES instrument.

Preliminary results show that the interpretation of spectral data in our study area can be confounded by a variety of factors, including overlaps of the spectral absorption features of different minerals. For example, areas interpreted spectrally to be sulfates have spectral features that overlap with clays. X-ray diffraction data and thin section analysis confirm that many of the samples indeed contain complex mixtures of evaporites and silicate minerals. In other cases, X-ray diffraction data confirms the presence of minerals identified spectrally, but those same minerals do not show up in laboratory spectra. Evaporite spectral signatures, especially those of chlorides, tend to be obscured by the silica and water present in playa minerals. To get an accurate picture of ground truth, thin sections will be analyzed to quantify the relative abundances of minerals in each sample. A spectral library of common evaporite minerals will also be compiled. When completed, MASTER and laboratory spectra will be re-analyzed to determine the precise resolution needed to for detect these minerals.

Further sample analysis will be needed to confirm the prediction that THEMIS resolution (100 m/pixel) is sufficient to detect and identify evaporates from Mars orbit. In addition, we plan to incorporate near-IR spectral information for the Badwater Basin using Airborne Visible Infrared Imaging Spectrometer (AVIRIS) to simulate a hyperspectral near-IR spectrometer that is planned for the 2005 Mars orbiter. This will help us refine the analytical tools that will be used to detect minerals using data sets to be obtained by THEMIS.

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High Resolution Chemical Study of ALH84001

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We have studied the chemistry of a sample of the SNC meteorite ALH84001 using an environmental scanning electron microscope (ESEM) with an energy dispersive chemical analytical detector and a focused ion beam secondary ion mass spectrometer (FIB-SIMS). Here we present the chemical data, both spectra and images, from two techniques that do not require sample preparation with a conductive coating, thus eliminating the possibility of preparation-induced textural artifacts. The FIB-SIMS instrument includes a column optimized for SEM with a quadrupole type mass spectrometer. Its spatial and spectral resolution are 20 nm and 0.4 AMU, respectively. The spatial resolution of the ESEM for chemical analysis is about 100nm. Limits of detection for both instruments are mass dependent.

Both the ESEM and the FIB-SIMS instrument revealed contrasting surficial features; crumbled, weathered appearance of the matrix in some regions as well as a rather ubiquitous presence of euhedral halite crystals, often associated with cracks or holes in the surface of the rock. Other halogen elements present in the vicinity of the NaCl crystals include K and Br. In this report, elemental inventories are shown as mass spectra and as X-ray maps.

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Organization of P, S, and Fe Inclusions in a Freshwater Magnetococcus

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Magnetotactic bacteria are a heterogeneous group of motile, mainly aquatic procaryotes that align and swim along geomagnetic field lines. They are of interest to astrobiologists because of the magnetite crystals found in the Mars meteorite ALH84001 which share many characteristics with the magnetite produced intracellularly by magnetotactic bacteria. These bacteria are diverse morphologically, physiologically and phylogenetically, sharing a few key characteristics: 1) the presence of intracellular membrane-bound magnetic crystals (magnetosomes), usually but not always arranged in chains; 2) motility by means of flagella; and 3) microaerophilic or anaerobic physiology. The bilophotrichous (having two flagella bundles) magnetotactic cocci (MC) are ubiquitous in aquatic habitats but have proven extremely difficult to cultivate. Because only several marine strains have been isolated and grown in axenic culture, little is known about the physiology and the biogeochemical roles of the MC. We studied the composition and distribution of intracellular structures in an uncultured MC, designated ARB-1. To do this, a combination of light microscopy, environmental scanning electron microscopy (ESEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) were used.

Cells of ARB-1 were separated from sediments collected from Baldwin Lake (Los Angeles Arboretum, Arcadia, CA). They are large spherical to oblate spheroidal Gram-negative cells, ranging from 1 to 4 μm along the maximum dimension, which is perpendicular to the direction of swimming. Cells have two large phosphorus-containing inclusions that comprise a large percentage of the cell volume. Many smaller sulfur inclusions are located at the convex end of the cell. Most of the cellular Fe is present in the magnetosomes. These may be arranged as a clump at the concave end of the cell, near the two flagella bundles, or as chains, or as both a clump and chains. The magnetosomes were identified as magnetite (Fe_3O_4) by selected area electron diffraction (SAED) and high resolution TEM.

We saw a trend between cell size and organization of the magnetosomes. Smaller, more spherical cells were more likely to have chains than were larger, more oblate cells. This may indicate different populations of cells, or it may be attributed to variations in cell growth cycle. The size distribution (length) of magnetosomes in chains was similar to that of magnetosomes in clusters, except that there was a larger size range for clustered magnetosomes. Magnetosomes from ARB-1 cells average 82 nm in length. If plotted on a graph of length as a function of aspect ratio, they fall within the single domain region of the plot. If compared with the size distributions of magnetite from ALH84001 and magnetosomes from the cultured magnetotactic vibrio MV-1, the magnetites produced by ARB-1 cells are, on average, larger and have a wider range of aspect ratio.

ARB-1 cells have a specific organization of the P, S, and Fe inclusions. The P inclusions always occupy the majority of the cell volume and separate the S inclusions from the disorganized clumps of magnetosomes and the flagella bundles. The P inclusions may contain polyphosphate, which could play several roles in motility, adaptation to stress, growth and division, buoyancy, and energy. The S inclusions might be a way to store S, a potential energy source, when the cells move from sulfide to oxygen zones. The consistency of P, S, and Fe organization in ARB-1 cells suggests that these inclusions have some specific and interactive functions.

Laboratory Studies of Hydrocarbon Nucleation on Tholin Particles and Thin Organic Films: Application to Titan's Atmosphere

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Titan, Saturn's largest satellite, has a thick nitrogen/methane atmosphere. In Titan's lower atmosphere, methane is saturated or supersaturated with respect to nucleation and may form clouds. To better characterize the properties of Titan's methane clouds we have measured the saturation ratio required to obtain butane nucleation, S_{crit} , on Titan tholin material and organic films. We find a critical saturation ratio for butane on tholin particles of $S_{\text{crit}}=1.40$, suggesting high supersaturations are required for nucleation. If methane is similar to butane, we expect high supersaturations of methane as well. This could favor the formation of a small number of large particles, consistent with recent measurements of methane rain on Titan.

A New Molecular Recognition Instrument for Astrobiological Applications

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Protein Chip-based molecular recognition technology is being developed as a method for detecting life in environments here on Earth and on the surfaces of planets and other solar system bodies. The Ciphergen Biosystems ProteinChip Reader (PBSII) is dependent on the surface chemistry of small chips to **selectively** capture **femtomole** amounts of **complex mixtures of organic molecules** for molecular weight determination by time of flight mass spectrometry. The surfaced-enhanced chips spatially orient molecules that are bound to them, such that they are more efficiently uncoupled and ionized for mass spectral analysis. Nanograms of organic matter dissolved in 1-2 microliters of buffer solution are placed on the chip and allowed to interact and bind. By using different chips, experiments can be designed to recognize a complex combination of molecular markers by selecting a series of chip surface chemistries to pull apart complex mixtures. It is also possible to determine the chemical nature of molecules with unknown chemical composition or structure by combining molecular weight determination, chemical binding information, and further chemical testing on the surface of the chip.

Proteomics: We will describe experiments to determine the protein profile of *Shewanella putrefascens*, a microorganism that is commonly isolated from geochemical gradient zones in which dissolved oxygen levels range from fully oxic to completely anoxic (Myers and Nealson, 1988; Tsapin et al., 1994). The genome of *Shewanella* has been sequenced in a DOE-funded project by TIGR, and over 70 protein or peptide chains have been identified in the organism. In our experiment with the ProteinChip Reader, ~2 mg dry weight of *Shewanella*, grown oxically on fumarate, was lysed in 1 ml of 0.1% Triton X-100 buffered by 0.1 M phosphate buffered saline (pH 7.4) (PBS). 2 µl of sample was allowed to chemically bind onto the surface of the chip for 30 minutes. Following binding and washing steps, replicate analyses of the chip detected 62 peptides or proteins from 754 to 237,954 daltons, some of which corresponded to molecular weights of protein identified from the genome. Based on the molecular weight of molecules of this size class and the amount of material in the starting solution, it is estimated that the instrument detected proteins in the lower picomole to higher femtomole range. Error for externally calibrated samples is (0.2%) in the range of 10,000 to 300,000 daltons.

Geochemical Studies: SELDI is an elegant technology that works well with freshly produced molecules and cell cultures. Extending this type of work to the geochemical environment, however, brings on a whole new set of concerns. In designing an *in situ* instrument for searching for life on Mars, geochemical considerations are paramount, because there is a much greater likelihood that if life existed on Mars, it arose early in the planet's history and may not be extant today. We will describe early work on the aspect of identifying unambiguous signatures of biological molecules in geochemical samples, as a stepping stone to developing capabilities that will be needed for extraterrestrial samples. On Earth, as would likely be true in an European ocean, the bulk of organic C molecules in the world's oceans are found dissolved in seawater. However, the chemical composition of dissolved organic matter (DOM) is complex and poorly understood, making it a good proxy to what might exist on Europa or Mars. As a test and demonstration of the power of SELDI technology to provide new information about complex mixtures, we targeted one of the recent debates about oceanic DOM. Studies have shown that DOM is comprised of some very old C many thousands of years old. A significant portion of DOM, however, has been formed recently. This younger material is directly linked to exudates originating from living organisms. Carbohydrates comprise the bulk of identifiable DOM with amino acids and their degradation products as the remainder. The compositional picture of DOM is much more complex than simple, biological molecules.

We used SELDI technology to determine the molecular weight distribution of organic molecules found in DOM to see whether large proteins or microbial cell wall fragments could be detected in DOM (<0.2 microns and >1,000 daltons) from the Equatorial Pacific Ocean (100 m depth) and from a riverine-derived filtrate (< 0.2 microns). Despite the very small amount of sample available and the challenging matrix, SELDI was able to provide exceptionally specific molecular-level results:

- The molecular weight distribution of the samples was in the range of 800 to 6,000 daltons. No material was detected between 10,000 and 100,000 daltons.
- A set of fourteen peaks was found in both the riverine and oceanic DOM.
- The riverine sample had the highest molecular weight peak at 6,000 daltons. This broad peak indicated a glycoprotein or other carbohydrate-bound moiety.
- The oceanic DOM sample had a series of molecular fragments in the range of 1,200 to 2,300 that were unique to this sample.
- Both samples had a suite of peaks that corresponded to a class of compounds with subunits in the range of 200-230 daltons.

The molecular weight distribution precludes any intact proteins in the sample. The molecules between 1000 and 6,000 daltons could be explained by units of microbial cell walls. Last and most important, the SELDI technique identified a **biosignature** in both of the samples—the common 14 peaks. And, it identified an additional biological source in oceanic DOM, not found in the riverine sample. SELDI was able to pull from a tiny amount of a very complex mixture a range of specific, unambiguous molecular structures. It was able to provide this very detailed molecular information much more rapidly, on far smaller samples, and with much less ambiguity than existing techniques that had been used before. This experiment shows that this technology will be extremely powerful for studying Martian soils or water from European oceans.

Astrobiology with ESA Science Missions

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Key questions of astrobiology can be addressed by several space missions from the ESA Science Horizons 2000 Programme, such as:

- How do solar and stellar systems form ?
(with ISO, FIRST, SMART-1, Rosetta, Colombo, Gaia)
- Geological evolution of terrestrial planets
(with Living planet, Mars-express, SMART-1, Bepi-Colombo to Mercury)
- Interstellar Complex organic chemistry
(with ISO, ISS/EXPOSE, FIRST, Rosetta)
- Co-evolution of Earth-Moon, impacts life frustration
(with SMART-1, Bepi-Colombo)
- How to detect other solar systems and habitable zones
(with space photometry, COROT, Eddington, Gaia, Darwin)
- Early Earth and alternative environments
(Huygens/Cassini and Mars-express)
- Signature of biosphere and photosynthesis evolution
(living Planet missions, Darwin)
- Water on Mars
(with orbiter instruments on Mars Express)
- Exobiology lander experiments
(with Beagle-2 lander on Mars-Express)
- Study of biomarkers and delivery of organics
(with Mars-express and future missions)

We shall review how the results from these ESA missions can be exploited in synergy to contribute to progress in astrobiology, and the perspectives for the next phases of solar system exploration, and life expansion beyond Earth.

AFM and XPS Analysis of Fossilized Microorganisms

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Identification of potential fossilized microorganisms from Mars will require an interdisciplinary approach combining a variety of methods. The hypothesis of our research is that x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), used in combination, can increase significantly our ability to image and recognize microbial fossils, and in particular to understand the phylogeny and physiology of microorganisms of primitive environments. To this end, our primary objective is developing microfossil-specific applications of AFM and XPS. AFM is a non-destructive, high-resolution surface imaging technique that relies upon several surface/tip interactions (e.g., electrostatic, Pauli exclusion forces, Van der Waals interactions, frictional forces). Although AFM is most commonly used to map surface microtopography, advances in AFM technologies such as Phase Imaging, Force Modulation, and force-curve measurements using different tip materials, are allowing some degree of compositional sensitivity. XPS is a surface analysis technique with an analysis depth of approximately 10 nm. This technique involves bombarding a solid sample with x-rays and resulting in the emission of electrons (photoelectrons). The energy of the photoelectrons can be used to identify not only the elements present, but the chemical state of the elements. The particular XPS we are using is capable not only of point analysis, but of surface composition mapping. AFM and XPS have unique capabilities that compliment each other (resolution, surface sensitive, chemical

signatures, etc.). Neither technology has been used previously in microfossil studies. Therefore, we are comparing XPS and AFM to more commonly used technologies (optical microscopy, scanning and transmission electron microscopy – SEM and TEM), using fossils of increasing age. A second objective is to gain greater understanding of the fossilization process itself, with respect to the fossilization of individual cell components and macromolecules (membranes, DNA, ribosomes, etc.).

We have chosen the cyanobacterium *Calothrix* as a model system. These photosynthetic organisms form filaments of 10-30 μm diameter which are easily identifiable using a low-power microscope. These distinctive structures can be identified in active hot-spring environments, but also are found in fossils derived from these environments. Visually identifiable *Calothrix* have been found in fossil assemblages ranging from a few tens of years up to 350 million years in age. Samples covering this entire range are available from Dr. J. Farmer (Arizona St. Univ.) for this study. As a preliminary systematic case study, three different types of *Calothrix* samples were analyzed: freshly dried onto glass slides, approximately 50-100 year-old silica sinters, and approximately 3 Ma silica sinters. The sinters were collected (by Dr. Jack Farmer) from hot springs deposits around Queen's Laundry Terrace, Sentinel Meadow, Yellowstone National Park, USA (50-100 year-old) and from McGinness Hills, central Nevada, USA (3 Ma), where *Calothrix* normally thrive. As a first step to analysis, an epifluorescence microscope was used to locate probable areas of fossilized microorganisms. Photomicrographs were taken of the sample surfaces using several excitation wavelengths. These photomicrographs served as maps for relocating sample areas to be analyzed by AFM in the Department of Geology and by XPS in the Department of Chemistry at Kent State University. Both AFM and XPS analyses were performed on the same sample areas.

Due to the increasingly rough surfaces of the older samples, AFM imaging was very difficult; however, a variety of surfaces were successfully imaged and are currently being interpreted. A preliminary XPS survey was obtained from the freshly dried sample, the resulting spectra showed peaks indicative of biogenic components. XPS results from the 3 Ma sample show a correlation between C and N (possible traces of biogenic material) intensities and Si and O (sinter material) intensities. Furthermore, the binding energies and photopeak shapes in the high energy resolution spectra informed us about the chemical environment. Basically, there is evidence for several C species, the N is consistent with some type of C-N bond, and the Si in the rock is reasonable for SiO_2 . XPS analysis of visibly fibrous and non-fibrous areas of the 100 year-old sample also indicate correlation between elements associated with biogenic activity (C, N, Fe) and specific sample locations. In one instance, an area presumed to be primarily inorganic rock material (visibly non-fibrous) actually turned out to contain some biogenic elements and patterns, thus showing that although the biogenic material may not be optically or morphologically obvious, XPS has the capability to assist us in identifying biogenically-active areas. Our ability to image the samples at high resolution by AFM and XPS demonstrates that these techniques should prove useful, especially when applied in a systematic fashion, integrated with microscopic and analytical approaches.

Mars Volatile and Climate History: Relevance to Life

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The possibility that life might exist at present or have existed in the past on Mars depends strongly on the abundance, distribution, and availability of water. In turn, the history and distribution of water is strongly coupled to the martian climate. These issues are inherently interdisciplinary, and couple measurements and processes related to the deep interior, the crust, the surface, the bulk atmosphere, the upper atmosphere, and interactions with the solar wind and escape to space. We have integrated observations from this wide variety of relevant disciplines that relate to martian climate and water, emphasizing recent Mars Global Surveyor and martian meteorite analyses, in order to construct a self-consistent view of the history of volatiles, climate, and water. While the result is not entirely unique, we are able to provide strong circumstantial evidence as to the nature of the martian environment through time. The major relevant observations are described below, followed by the integrated perspective of martian volatile and water evolution.

Nature of the early climate and connections to geology and geophysics:

1. Valley networks and high erosion rates on ancient surfaces suggest a warmer and wetter early climate.
2. Valley networks tend to follow slopes related to formation of Tharsis, indicating that the bulk of Tharsis formed early. Tharsis volcanism likely was a source of CO₂ and H₂O to the early martian atmosphere, and may have sustained the early climate.
3. The formation of Tharsis warped the surface, and much of the fluvial activity throughout time is connected to the circum-Tharsis trough, indicating a strong connection between the geophysics and climate.
4. Valley networks also coincide with locations of remnant magnetic anomalies, suggesting either a temporal connection or cause-and-effect, although either connection cannot be easily understood.

Processes and timing in evolution of the atmosphere:

1. Early impacts can eject atmosphere, and the number of observed craters is consistent with loss of 50-90 % of an early atmosphere.
2. Ratios of stable isotopes indicate stripping of the atmosphere to space by the impinging solar wind, with loss of up to 90 % suggested.
3. Gas trapped in ALH84001 may represent atmosphere trapped 3.9 b.y.a. It shows essentially no isotopic fractionation, indicating that loss of the atmosphere to space occurred subsequent to that time.
4. As a magnetic field would protect the atmosphere, turn on of solar-wind stripping would only occur as an intrinsic magnetic field ceased and presumed-globally-distributed remnant anomalies were erased. The timing inferred for these processes is consistent with the inferred timing of loss to space.
5. Substantial quantities of carbonate or sulfate minerals that could be a sink for an early atmosphere have not been identified on the surface, although they could be buried or distributed throughout the crust.

Geological evidence for crustal liquid water:

1. Catastrophic flood channels occur episodically throughout martian history, requiring large crustal reservoirs of liquid water throughout history.
2. Weathering products are present in the martian meteorites, indicating that liquid water has circulated through the crust. Their presence in the younger meteorites indicates that this has occurred late in geological history.
3. Coarse-grained hematite is observed at the surface, and is best explained as resulting from weathering in previously subsurface hydrothermal or aqueous systems.
4. Geologically young gullies and seeps are observed that are best explained as having been carved by liquid water present relatively near to the surface.

What's the bottom line?

Self-consistent scenarios for the history of martian climate and volatile abundance can be constructed from these observations: During some period of the Noachian the climate was sufficiently clement to allow significant fluvial erosion. This warm period, which terminated abruptly at the end of the Noachian, likely involved outgassing by volcanism associated with ancient highlands and Tharsis, subsequent turn-on of solar-wind stripping of atmosphere associated with the turn-off of the intrinsic magnetic field and “erasure” of some local magnetic anomalies, and loss of volatiles to space by solar-wind stripping and by impact erosion. There is clear evidence that loss of the early atmosphere involved each of impact erosion, solar-wind stripping, and formation of subsurface carbonates, although the relative importance of these processes is not known.

Iron Isotope Measurements in Meteorites and Terrestrial Rocks

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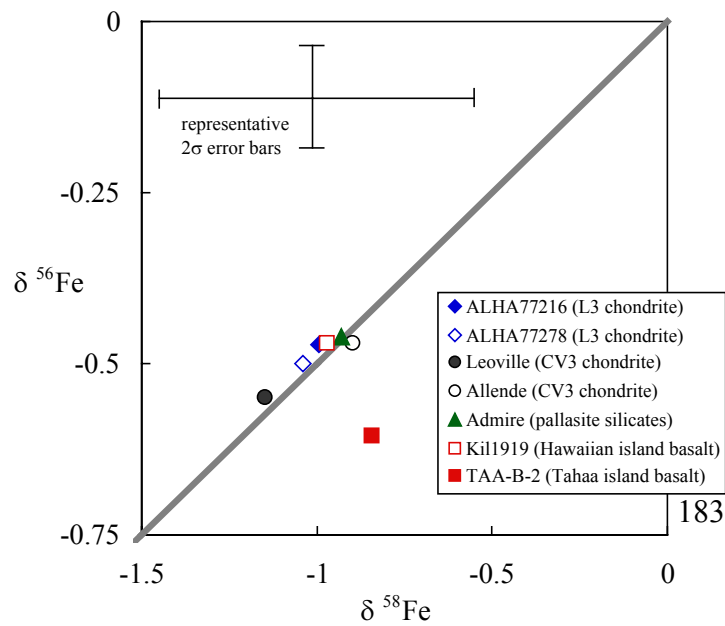
The geochemistry of iron is the subject of increasing interest within the astrobiology community because metabolic reactions in microorganisms may change the isotopic composition of iron to a greater extent than abiotic processes [1]. If correct, iron isotopes provide a way to distinguish biological from abiological mass fractionation, potentially permitting identification of fossilized evidence of microbial activity in natural samples.

To date, most iron isotope analyses have been performed on terrestrial rocks. Meteorites from asteroids provide a useful alternative setting in which to study abiological mass fractionation because they are devoid of biological processing. Variations in the isotopic composition of iron in meteorites can plausibly arise from the presence of unequilibrated presolar materials, temperature sensitive isotope exchange reactions, and kinetic processes. Such effects are interesting in their own right because they reflect physical and chemical conditions existing at the time the meteorite parent bodies formed.

We have developed a technique for precisely measuring the isotopes of iron using multi-collector inductively coupled plasma mass spectrometry (ICP-MS) [2]. Our initial emphasis is on the analyses of meteoritic material where we hope to address a number of problems relating to the origin and evolution of planetary bodies as well as the geochemical behavior of iron itself.

The analytical procedure includes acid dissolution of rock samples, followed by iron separation on an anion column. Purified samples are run on a multi-collector ICP-MS. The argon source plasma is operated at reduced power (so-called cold plasma mode) to eliminate ArN^+ and ArO^+ , which otherwise would interfere with measurements of ^{54}Fe and ^{56}Fe . Sample analyses are alternated with measurements of a pre-purified standard (Puratronic iron), dubbed 'P1'. Repeat analyses of isotopically spiked standards suggest that the external reproducibility of the technique is comparable to the typical in-run precision ($\delta^{56}\text{Fe} \sim \pm 0.1$ and $\delta^{58}\text{Fe} \sim \pm 0.6$ at the 2 sigma level).

The figure shows the results of several analyses of bulk meteorite compositions and two analyses of terrestrial ocean island basalts. Data are plotted on a three-isotope diagram,



with $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{58}\text{Fe}/^{54}\text{Fe}$ ratios expressed as deviations in parts per 10^3 from the composition of the P1 standard on the ordinate and abscissa, respectively. Thus the composition of P1 lies at the origin of the plot on the upper right. Representative uncertainties (2σ) are shown in the upper left of the figure. The gray line represents the approximate array of iron compositions that can arise from mass dependent fractionation assuming all samples have the same starting composition. The availability of two isotope ratios permits the resolution of true isotopic mass fractionation from isotope anomalies that might occur in meteorites. Monoisotopic additions to ^{58}Fe , for example, would plot significantly to the right of the mass fractionation line. Such effects would not be resolvable if only two isotopes of iron were measured instead of three.

All data occupy the same region of the plot indicating they have a similar iron isotopic composition. This reinforces the view that meteorites have the same bulk iron composition as the Earth and suggests that core formation on the Earth did not significantly fractionate iron isotopes. The data cluster is shifted from the P1 composition by about 0.025 % per amu. Evidently the P1 iron standard was mass fractionated, favoring the heavy iron isotopes, by some industrial process during purification and preparation.

Having confirmed the usefulness of the cold plasma ICP-MS technique, future work will focus on specific problems relating to the geochemical behavior of iron in meteorites as well as in ancient terrestrial sediments. Of particular interest is the degree of mass fractionation during high temperature processes occurring in the solar nebula and during planetary differentiation.

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Isotopic Biosignature in Calcite Formed During Weathering of Basalt: Implications for Past Life on Mars, Early Life on Land, and ALH 84001

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Enormous variations in oxygen and carbon isotopes have been observed in carbonate developed as a weathering product (caliche) on < 1 Ma basalts in 3 volcanic fields in Arizona (Fig. 1).

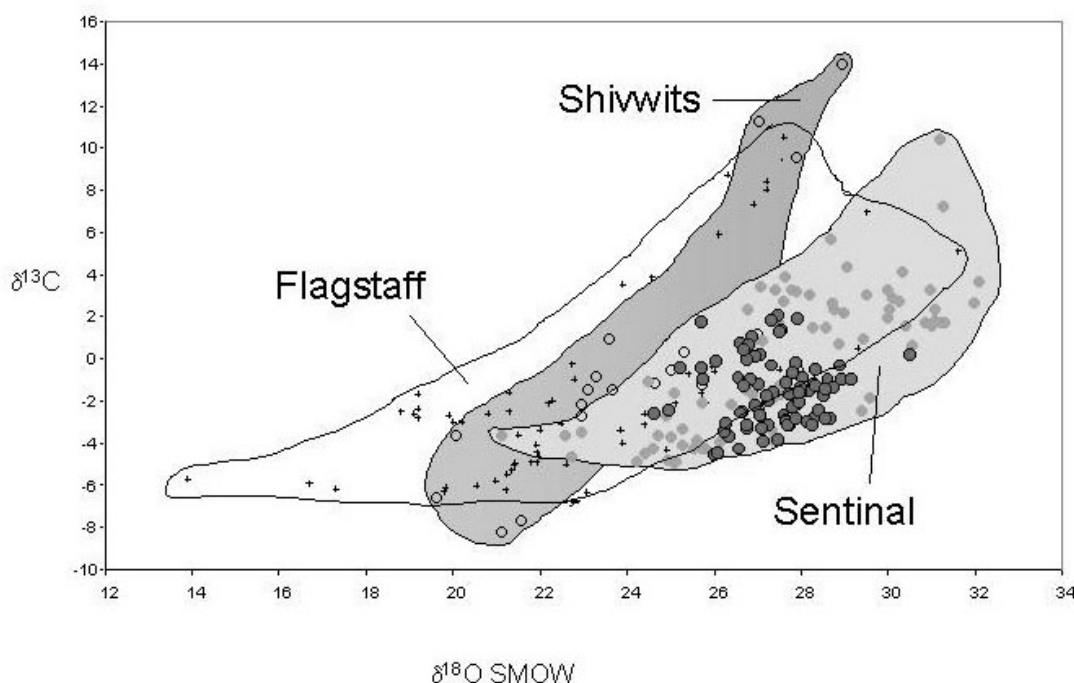


Fig. 1 Isotopic variations in Flagstaff, Shivwits, and Sentinal Volcanic Fields, Arizona

These variations are larger than those found in all terrestrial limestones and dolostones, everything taken together. Within each volcanic field, $\delta^{18}\text{O}$ is broadly co-variant with $\delta^{13}\text{C}$ and increases as $\delta^{13}\text{C}$ increases. In all cases, the most ^{18}O and ^{13}C enriched samples (upper right ends of the arrays in Fig. 1) are for calcite developed on pinnacles, knobs, and flow lobes that protrude above tephra, rubble, and soil. These have apparently stood in the air since eruption and have never been exposed to the soil atmosphere environment. All of the ^{18}O and ^{13}C depleted samples (lower left ends of the arrays in Fig. 1) are currently covered by soil or tephra and have been long exposed to soil atmospheres. Carbonate development is extensive for the covered samples and is sparsely developed on and within the subaerial samples. Calcite in isotopic equilibrium with Flagstaff meteoric waters has $\delta^{18}\text{O}$ values of +19‰ to +23‰. The pedogenic, lower

left end of the Flagstaff array is clearly soil calcite which formed in local meteoric waters and has low $\delta^{13}\text{C}$ characteristic of microbial soil CO_2 . Calcite at the upper right end of the Flagstaff array has clearly formed from ^{18}O -rich evapoconcentrated meteoric waters that dried out on surfaces after local rains. The enormous ^{13}C enrichment is due either to removal of ^{12}C by photosynthesizers in the evaporating drops or to kinetic isotope effects associated with evaporation. The elongated data array is thus a mixing curve for calcite that forms in the atmosphere with that formed in soil rich in microbes. The same pattern is observed in the 2 other volcanic fields and is interpreted similarly.

Individual vugs and amygdules filled with calcite display the same elongated data array on a smaller scale. Calcite thus initially forms with the isotopic signature of evaporation and is subsequently overlayered during burial by calcite carrying the isotopic signature of the soil environment. The enormous change in carbon isotope composition as calcite growth occurs is a unique signature of biology.

Implications:

Mars: The martian surface has local basalt flows and is elsewhere littered with basaltic boulders, breccia fragments, and wind-blown particles. If it ever rained on Mars, carbonate can be expected to have formed as in the examples above. If microbes were present, a huge zonation of carbon isotopes should be present as in the terrestrial examples. It is the change and the co-variation with $\delta^{18}\text{O}$ that is significant. We don't know $\delta^{13}\text{C}$ of the martian carbon reservoir, so measurements of $\delta^{13}\text{C}$ alone cannot prove the presence of past biologic activity. However, an array similar to any of those shown above on Mars would be a strong indication that microbial life had been present and left its isotopic imprint.

Life on Land in the Precambrian. The oldest microfossil evidence of terrestrial organisms on Earth is 1.2 Ga. Geochemical arguments have been made that the land surfaces were already populated in the Archean. Paleocaliche developed on Precambrian basalts provide a new opportunity to explore the early occupation of land. Carbon isotope variations as large as those shown above would be a strong argument for biological activity during the basalt weathering episode.

ALH 84001: The oxygen isotope variations in carbonate in this famous meteorite are almost the same as the range shown in Fig. 1 for the terrestrial examples. The large variations have been interpreted as precluding a low temperature origin. However, it is clear from the present results that these variations are compatible with a low temperature origin. $\delta^{13}\text{C}$ values have been published, but simultaneous measurements of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ on the same material have not been reported. This should be done because a data array similar to one of those shown in Fig. 1 (albeit displaced to higher or lower values characteristic of the overall martian isotopic reservoir) might be present if microbes were present during carbonate precipitation.

“Follow the Water, Beware the Brine”: Astrobiological Implications of Aqueous Seeps on Mars

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The slogan “Follow the water” has become a guiding principle in Astrobiology. Consequently, there is considerable excitement over the discovery on Mars of arrays of small erosional gullies descending from specific levels along escarpments because these have been interpreted as recent seeps of liquid water. The presence of such seeps at 120 localities on Mars gives rise to the possibility of vast reservoirs of subsurface martian water and the possibility that microbial life is, or was, present in these reservoirs. The problem is that it is simply too cold on Mars for liquid water to flow across the surface or for aquifers to exist at shallow depths in the megaregolith. However, highly concentrated brines can have exceptionally low freezing points and are also remarkably susceptible to supercooling. Brines with freezing points lower than average current martian surface temperatures (ca. -65°C) are found on Earth, so concentrated brines are excellent candidates for the martian seep fluids if there is a mechanism by which they could have developed on Mars.

The conventional view is that on Earth, Mars, and Venus, H_2O was outgassed following accretion. Cl is a volatile element that does not fit readily into silicate minerals and would therefore have outgassed as HCl along with the H_2O . In the earliest hydrospheres, HCl was therefore an important dissolved constituent. Later leaching of Na from the earliest crust produced largely NaCl-bearing oceans. On Venus, the initially high CO_2 levels resulted in a runaway greenhouse in which most of the water was lost via gravitational escape. On Earth, greenhouse temperatures were moderate enough to allow retention of the early ocean, and it has persisted. The Earth’s earliest ocean appears to have had a salinity 1.5 – 2 X the modern value and that salinity declined with time as evaporite and brine deposits became sequestered on evolving continental platforms. If the Cl/ H_2O ratio of outgassed volatiles on Mars was similar to that on Earth, then the earliest martian ocean would have had a similarly high salinity. However, the absence on Mars of continents with huge sedimentary basins sequestering giant salt deposits precludes using the subsequent development history of terrestrial brines as an analog for martian brine.

Photodissociation of water vapor in the upper atmosphere of Mars produces hydrogen that is able to escape from the planet much more easily than it does from the more massive Earth. Based on the high D/H ratio of water vapor in the current atmosphere, 50-

95% of the original martian hydrosphere was lost by this mechanism. Loss of water to space leaves the residual hydrosphere enriched in its dissolved constituents. The early martian hydrosphere therefore necessarily evolved into a NaCl brine. This brine became pore fluid in a megaregolith composed of high surface area particles (fractured and fragmented glasses, impact breccia, pyroclastic debris, ash sheets, melt sheets, and small rock fragments) of basaltic or komatiitic composition. Chemical interaction with these particles was inevitable and would have converted the NaCl brine into a concentrated Ca-Mg-Na-Cl brine with numerous other dissolved constituents. Mars subsequently froze, and the subsurface brines underwent eutectic freezing to produce a mixture of H₂O ice, salts (mostly NaCl•2H₂O and CaCl•6H₂O), and highly concentrated brine. Such brines could still be seeping out of escarpments and readily account for the remarkable and otherwise perplexing outflow gullies. Eutectic brines therefore logically follow from current ideas regarding initial outgassing of volatiles, atmospheric water loss, and later freeze-down.

If the scenario above is correct, past and any present surface and ground waters on Mars should have been primarily brines with concentrations greater than that of modern terrestrial sea water. During the “warm, wet” early history of Mars, fresh water could have occurred locally as rain, runoff, and groundwater reservoirs. Such precipitation-derived water would have been very limited because erosional channels attributed to runoff (as opposed to catastrophic outflow) are not developed planet-wide. However, freeze-down of the planet should have generated widespread and extensive amounts of subsurface H₂O ice cements as a consequence of eutectic freezing. Later melting of this ice by igneous activity could have produced liquid H₂O in convecting cells and possible hydrothermal springs. On the other hand, such geothermal heating would also mobilize eutectic brines and re-melt ice-brine-salt eutectic mixtures where they were still physically associated. Mixing of these diverse fluids during hydrothermal circulation combined with dissolution of megaregolith salts would probably prevent sustained hydrothermal reservoirs of dilute H₂O for any significant length of time.

In view of the above, we submit that ideas regarding the possible origin and early evolution of life on Mars must confront the issue of whether such life is enhanced or retarded by solutions with salinities greater than that of modern terrestrial sea water. Are there any halophilic bacteria deeply rooted in the rRNA tree? Is the formation of prebiotic molecules, membranes, and primitive cellular structures facilitated or inhibited by highly saline solutions? If salinity lower than that of modern terrestrial sea water is more optimal, where on Mars might such limited amounts of fluids have accumulated and become sequestered for early evolution of life? These questions also apply to the origin and evolution of life on Earth or on any planetary object with similar initial Cl/H₂O ratios.

So, follow the water, but beware the brine!

Consequences & Artifacts: Terrestrial Findings and Martian Analogues of an Air-Water Interface

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Natural consequences of the terrestrial bubble-aerosol (bubblesol) cycle are objects with properties fascinatingly akin to those of ‘nanobacteria’: in particular the basic morphology (spheres and sausages), gross chemistry (suites of organics along with metals), and size distributions (nanometers to microns). Whether of biological or bubblesol origin, these striking similarities reflect the universality of the chemical physics involved in the interactions of charge-polarized organic amphiphiles at an air-water interface.

The contemporary terrestrial bubblesol cycle can include bubble formation, the adsorption of surface-active materials, bubble dissolution, and bubble bursting. The non-equilibrium energetics of bubble bursting is coupled to the formation of aerosols and their subsequent roles in atmospheric condensation. The bubblesol cycle provides an infrastructure for the concentration and transport of organic compounds, metal ions, and mineral catalysts through a rapid sequencing of hydration-dehydration reactions. Additionally the bubblesol cycle creates and seeds the principle nodes of heterogeneous organometallic chemistry in both the atmosphere and the ocean.

On the contemporary Earth, in both particle number and total mass, bubble-generated aerosols and their atmospheric progeny are the *largest transporters* of organic matter between the atmosphere and ocean. Hence on an early Earth this geophysical-chemical cycle seems likely to have played a critical role in prebiotic chemical self-organization. More generally, whether we are considering Earth, Mars, Titan, or Europa... in the search for life and its origins the bubblesol cycle, its processes, and its resulting mass objects must be taken into account.

With respect to current Mars mission planning:

- The finding of bubblesol-generated objects (of Martian origin) in Martian meteorites or on Mars itself is *prima facie* evidence for the existence of a complex Martian hydrology cycle capable of gathering, concentrating, and transporting organics.

- The presence of such bubblesol objects in (or from) an extraterrestrial location implies substantial environmental opportunities have existed for the support of prebiotic chemical evolution.
- On a tectonically simple early Mars (with only intermittent surface liquid water), the bubblesol cycle may have been the only initiator and supporter of the rapid cycles of concentration, hydration, and dehydration necessary for organic polymerization in 'bulk' quantities.
- Any life-searching Mars missions (or interpretations of Martian objects having come to Earth) must discriminate between the fossils of living systems at the nanobacterial scale and potential artifacts of the bubble-aerosol cycle necessarily created on any planet, planetoid, or satellite having both liquid water and amphiphiles.
- Additionally, IF bacteria (with surface active membrane elements) have existed on Mars, and were coupled to a surface liquid water environment, then these same bubblesol processes could have been the principle mode of bacterial concentration and aerial transport. In analogy to current terrestrial processes the larger of these bubblesol-generated objects (in their hydrated state) could easily have transported such bacteria across a mostly arid planetary surface. This may have been critical for 'colonization', and could also explain the deposition and subsequent fossilization of "micro-clumps" of such bacteria in micro-environments much removed from their origin.

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Isotopic Analysis of High and Low Temperature Components of Tagish Lake: Anatomy of a New, Very Primitive Carbonaceous Chondrite

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The Tagish Lake meteorite has properties intermediate between CI and CM meteorites, and may represent a new type of carbonaceous chondrite [1]. In order to explore its origin, history, and possible astrobiological relevance, we present oxygen isotope analyses of relatively high-temperature (olivine) and low-temperature (carbonate) components of Tagish Lake.

Both conventional and ion microprobe oxygen isotope analyses are presented. About 600 mg of a “degraded” Tagish Lake sample (*i.e.*, a piece of a fragment collected after ~3 months on the frozen Tagish Lake bed; [1]) was gently crushed and mixed. A 100 mg aliquot of this homogenized sample was disaggregated via ultrasonication, filtered, and transparent grains $>50\text{ }\mu\text{m}$ in size were hand-picked, mounted and polished with ion probe standards. We determined oxygen isotopic compositions of 5 forsterites, and 2 intermediate composition olivines using the Cameca IMS 6f ion microprobe at ASU. One of the forsterite grains has a thin ($\sim 10\text{ }\mu\text{m}$) rim of intermediate composition olivine. In this case, both core and rim were analyzed. The analysis conditions were identical to those reported by [2].

Two additional aliquots of the crushed sample (99 and 198 mg) were used to determine the isotopic composition of carbonate at UCSD, following the methods of [3,4]. CO_2 was extracted by the phosphoric acid technique. Carbonates ranging from calcite to breunnerite (Fe,Mg carbonate) are reported in Tagish Lake [1]. To constrain the abundance and composition of these different carbonate minerals, the samples were extracted in sequential time steps at temperatures ranging from 25 to 150°C (Table 1) [5,6]. CO_2 was purified using gas chromatography and fluorinated to release O_2 , which was isotopically analyzed using a Finnigan MAT 251. Data from two aliquots of Orgueil are also reported for comparison. Uncertainties are estimated to be $\sim \pm 0.1\text{ ‰}$ for the carbonate $\Delta^{17}\text{O}$ values, and $\sim \pm 0.3\text{ ‰}$ on the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values.

The isotopic compositions of the Tagish Lake olivine grains range from $\delta^{18}\text{O}_{\text{SMOW}}$ of -17.0 to $+1.8\text{ ‰}$ and $\delta^{17}\text{O}$ of -14.6 to -0.9 ‰ (Fig. 1). The data form an array subparallel to, but slightly to the left (low- $\delta^{18}\text{O}$ side) of the line representing the compositions of

Allende CAIs. In all grains analyzed thus far, forsteritic olivine is more ^{16}O -enriched than olivine of intermediate chemical composition. In the zoned olivine grain, the forsteritic core is similar to other forsterites analyzed, and the intermediate composition rim is like other intermediate olivines analyzed, although slightly more ^{16}O -enriched. This difference between the rim and the other intermediate olivines could be the result of physical mixing of part of the ^{16}O -rich core under the $\sim 20\ \mu\text{m}$ diameter ion probe beam. The yields of CO_2 from different carbonate extraction steps demonstrate that dolomite is the most abundant carbonate in Tagish Lake, followed by breunnerite, and calcite. In total, we find 7-8 wt. % carbonate in Tagish Lake. The isotopic compositions of carbonate from Tagish Lake and Orgueil are reported in Fig. 2. The Tagish Lake carbonates have variable $\delta^{18}\text{O}_{\text{SMOW}}$ (+32.5 – +37.1 ‰) and $\Delta^{17}\text{O}$ (+1.4 – +2.0 ‰) values. The Orgueil carbonate $\delta^{18}\text{O}$ values also vary (+25.1 – +30.8 ‰), consistent with prior ion probe work [7], but the observed $\Delta^{17}\text{O}$ values are relatively constant (+0.3 – +0.5 ‰).

Findings of this work can be summarized as follows: (1) Although the data are limited, Tagish Lake forsterites appear to be consistently more ^{16}O -enriched (by a few ‰) than typical chondrule and isolated olivine from other carbonaceous chondrites. The comparison to CI and CM data is shown in Fig. 1, but the observation holds for olivine from CV and CR chondrites as well. (2) although carbonate is more abundant in Tagish Lake than in CI and CM chondrites (also found by [1]), the carbonates must be almost entirely $< 50\ \mu\text{m}$ in size, or they would have been found along with the olivine in the hand-picking of the sample. In this way, Tagish Lake more closely resembles CM than CI chondrites. (3) The $\Delta^{17}\text{O}$ values for Tagish Lake carbonates are significantly higher than carbonates from either CM or CI chondrites, and their $\delta^{18}\text{O}$ values are higher than all but a few CM analyses (Fig. 2). The $\Delta^{17}\text{O}$ values are the highest ever measured in chondrite carbonate. (4) Because the carbonate $\Delta^{17}\text{O}$ tracks that of the altering water, the data require that the water that interacted with Tagish Lake had a $\Delta^{17}\text{O}$ value of at least +1.9 ‰. This value is lower than (and therefore consistent with) the “High Water” value proposed in the two-reservoir (static) water-rock interaction model of Clayton and Mayeda [8], but higher than the “Low Water” value from [8] and the altering water composition discussed by Young et al. [9] in their flow model. (5) Within the context of the two-component interaction model, the higher $\Delta^{17}\text{O}$ of both the whole rock and carbonate in Tagish Lake compared to CM chondrite compositions (Fig. 2) is consistent with higher water:rock ratios in the Tagish Lake alteration relative to the alteration of CM chondrites.

In summary, although Tagish Lake shows some isotopic similarities to both CI and CM meteorites, it is not clearly affiliated with either group. This may support the idea that Tagish Lake represents a new, unique C2 chondrite [1].

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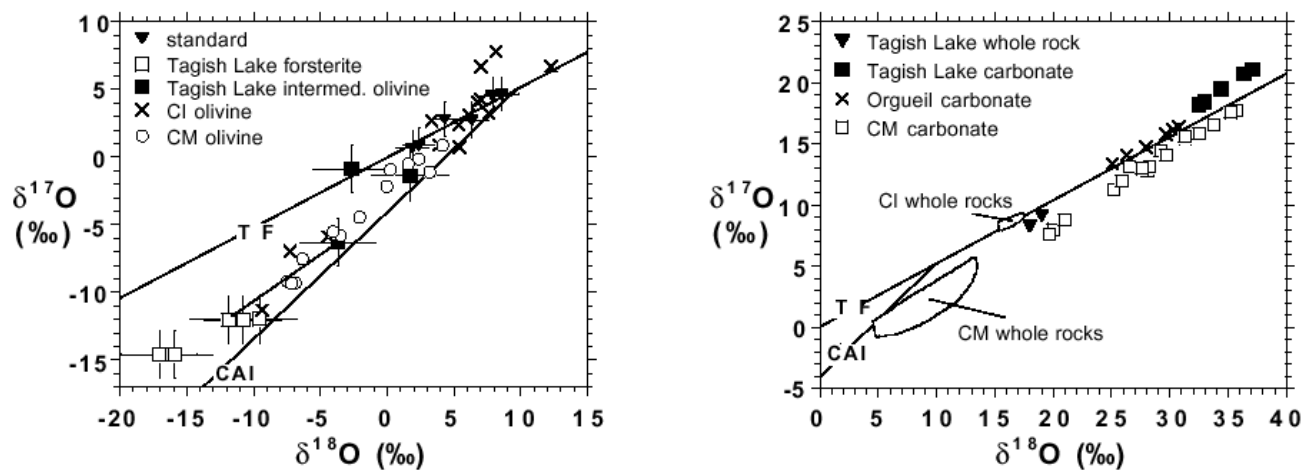


Fig 1. (left) O-isotopic composition of 7 olivine grains separated from Tagish Lake. Data for the ion probe standard (San Carlos olivine), and comparable olivine grains from CI and CM chondrites are also shown. The core and rim data from one highly zoned olivine analyzed are connected by the short line. Fig 2 (right) O-isotopic composition carbonates from Tagish Lake compared to carbonates extracted by the same approach from CI Orgueil and 5 CM chondrites [4].

Abiotic Versus Biotic Weathering Of Olivine As Possible Biosignatures

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We are investigating the weathering of silicate minerals by both purely inorganic, and biologically mediated processes using field-emission scanning electron microscopy (FE-SEM) and energy dispersive x-ray spectroscopy (EDS). By resolving surface textures and chemical compositions of weathered surfaces at the sub-micron scale we hope to be able to distinguish abiotic from biotic weathering processes and so establish a new biosignature applicable to the study of astromaterials including but not limited to the Martian meteorites [1]

Sterilized olivine grains (San Carlos, Arizona) no more than 1-2 mm in their longest dimension were optically assayed to be uniform in color and free of inclusions were selected as weathering subjects. Prior to all experiments surface morphologies and Fe/Mg ratios were determined for each grain using FE-SEM and EDS (Fig. 1a). Experiments were divided into two categories abiotic and biotic and were compared with “naturally” weathered samples.

For the preliminary experiments, two trials (open and closed to the ambient laboratory environment) were performed under abiotic conditions, and three trials under biotic conditions (control, day 1 and day 2). The open system abiotic trials used sterile grains heated at 98°C and 200°C for both 24 and 48 hours in 1L double distilled de-ionized water (Fig. 1b). The closed system abiotic trials were conducted under the same conditions but in a sealed two layer steel/Teflon “bomb” apparatus. The biotic trials used

sterile grains mounted in a flow-through device attached to a wellhead on the Columbia River aquifer. Several discolored, altered, grains were selected to document “natural” weathering surface textures for comparison with the experimental samples.

Preliminary results indicate there are qualitative differences in weathered surface textures among all the designed experiments. The olivine grains in abiotic trials displayed etching, pitting, denticulate margins, dissolution and clay formation. The scale of the features ranged from tens to a few microns with textures that remained relatively sharp and were crystallographically controlled (Fig. 1c). These results were comparable to that observed in the “naturally” weathered comparison/reference grains. Chemical analysis by EDS indicates these textures correlated with the relative loss of Mg and Fe cations by diffusional processes. In contrast the biotic results indicated changes in the etching patterns on the scale of hundreds of nm, which are neither sharp nor crystallographically controlled (nanoetching). Organisms, organic debris and/or extracellular polymeric substances (biofilm) were often in close proximity or direct contact with the nanoetching (Fig. 2).

While there are many poorly constrained variables in natural weathering experiments to contend with, such as the time scale, the chemistry of the fluids and degree of biologic participation, some preliminary observations can be made: (1) certain distinct surface textures appear correlated with the specific processes giving rise to these textures [2]; (2) the process of diffusing cations can produce many similar styles of surface textural changes; and (3) the main difference between abiotic and biotically produced weathering is the scale (microns versus nanometers) and the style (crystallographically versus non-crystallographically controlled) of the textural features. Further investigation into nano-size scale surface textures should attempt to quantify both textures and chemical changes of the role of microorganisms in the weathering of silicates. Additional experiments addressing nanoscale textures of shock features for comparison with the current data set.

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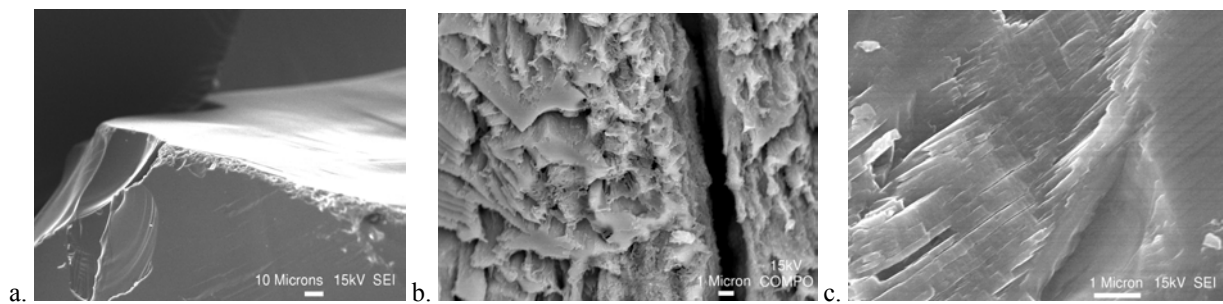


Fig. 1: a) An example of a pristine olivine grain after cleaning and sterilization. b) A backscatter image of an open system abiotic trial at 98°C for 48 hours. Clay formation is extensive and the relative abundance of Fe and O increases on the blades that jut out from the clays. c) An example of etching that occurs naturally in the San Carlos olivine.

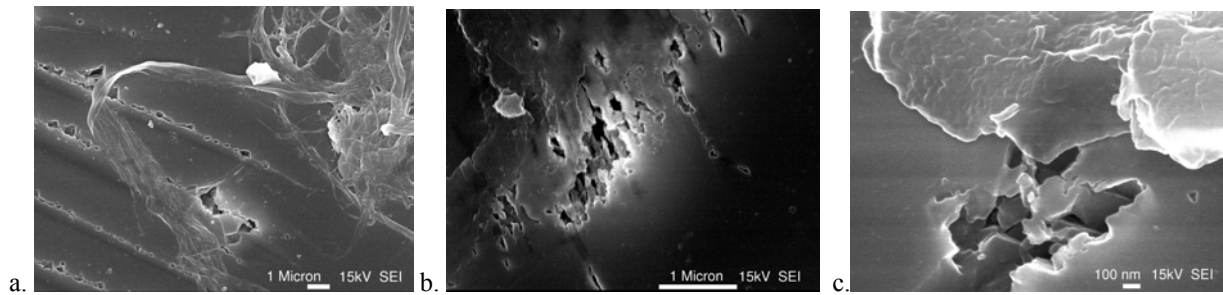


Fig. 2: a) Biofilm stretching into larger crystallographic pits. b) Nanoetching in close proximity to organism. c) An example of the correlation of shriveled organic matter and nanoetching. Small rounding and irregular etching inside of a larger earlier formed pit demonstrate nanoetching.

Thermal Desorption/GCMS Analysis of Astrobiologically Relevant Organic Materials

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Several macromolecular organic materials, both biologically-derived (type II kerogen and humic acid) and abiotic in origin (Murchison insoluble organic material, cyanide polymer, and Titan tholin) were subjected to thermal desorption using a Chromatoprobe attachment on a Varian Saturn 2000 GCMS system. Each sample was heated sequentially at 100, 200, and 300°C to release volatile components. The evolved compounds were then separated on a Supelco EC-1 dimethylsilica GC column and detected by the Saturn 2000 ion trap mass spectrometer.

The various types of macromolecular organic material subjected to thermal desorption produced distinctly different GCMS chromatograms at each temperature, containing fractions of both low and high chromatographic mobility. The relative amounts of detectable volatiles released at each temperature also differed, with type II kerogen and cyanide polymer containing the highest percentage of low-temperature components. In all the samples, the highest yield of released compounds occurred at 300°C. Only cyanide polymer evolved a homologous hydrocarbon series, suggesting that it is the only material among those examined that contains a truly polymeric structure.

Pyrolysis/gas chromatography/mass spectrometry has been used extensively for analysis of terrestrial organic macromolecular materials, and was also part of the instrument package on the Viking landers. Thorough analysis by pyrolysis usually employs temperatures of 500°C or higher, which for *in situ* analyses can be problematic given spacecraft power and materials constraints. This study demonstrates that heating of organic materials of astrobiological relevance to temperatures as low as 200-300°C for short periods releases volatile components that can be analyzed by gas chromatography and mass spectrometry. Even in the absence of full pyrolysis, useful chemical information on samples can be obtained, and materials from different biological and abiological sources can be distinguished.

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

Possible Biologic Features in Martian Meteorite Nakhla

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Controversy still rages over whether certain features in martian meteorite ALH84001 are biogenic and indigenous. Recent studies of the nanophase magnetite in the dark rims of carbonate globules and pancakes have made the case that a subpopulation of the magnetites are indistinguishable from magnetites produced within the cells of terrestrial magnetotactic bacteria strain MV-1 (1, 2). No nonbiologic process, whether laboratory or natural, is known to produce exactly this form of magnetite. If such magnetites were found in any terrestrial sample, they would be taken as clear evidence for biology. Others have also interpreted them as presumptive evidence for early life on Mars (3). As such, they are the oldest fossils ever found.

We have been studying another martian meteorite, Nakhla. This meteorite was an observed fall in June, 1911 near the village of El Nakhla, Egypt, and was collected soon thereafter. We have been studying subsamples from a British Museum specimen that had a nearly complete fusion crust before it was broken up recently in a clean bench at Johnson Space Center for allocation. We have surveyed some of these chips with Field-Emission Scanning Electron Microscope (FESEM) and petrographic microscopy.

Nakhla is an igneous rock, a clinopyroxenite containing augite, olivine, and a mesotaxis with feldspar, phosphates, magnetite, and other minerals. The rock also contains secondary minerals and phases, including carbonates, iron oxides, clay minerals, sulfates, chlorides, and amorphous or glassy material, which fill cracks and cavities and also appear to replace parts of the mesotaxis.(4, 5). Textural evidence is presented in these papers supporting the hypothesis that most, if not all of these secondary minerals were formed on Mars. Nakhla also contains significant organic material which ¹⁴C analysis indicates is at least 80% indigenous (6).

In some of the cracks filled with secondary minerals, small (~0.5µm) specks are visible in optical microscope images (Fig. 1). These specks are patchy in distribution, have a narrow size distribution, and are usually associated with carbonate, clay, or silica crack fillings. We propose that these specks may be fossilized bacteria from Mars. Lacking definitive evidence that they are truly fossilized bacteria, we term them bacteriamorphs. SEM examination of a number of small chips of Nakhla from both samples near the fusion crust and samples in the interior reveals a set of features which are the same size and shape as those observed in the petrographic microscope (Fig.2). These bacteriamorphs are of several types. Subspherical or coccoid forms are the most common, but elongated or rod-shaped bacteriamorphs are also present. Preliminary compositional data from energy dispersive x-ray analysis suggests that some of these

features are richer in Fe and O compared to the surrounding matrix. In addition, some of the patchy material may be fossilized polymeric material originally generated by the bacteria. EDX analyses indicate it is considerably enriched in Si compared to the matrix, and could conceivably be SiO₂.

Many of the forms are partly embedded in a matrix, and some are mostly covered. The chips contain a number of small features which resemble fossilized bacteria from terrestrial samples. (Fig.2). The morphologies of most of the biomorphic features in Nakhla are similar to known fossilized bacteria and associated features formed in Columbia River Basalt, using microbe-bearing water from subsurface aquifers (7). Additional work is underway to examine the Nakhla bacteriamorph features in the transmission electron microscope (TEM). These features could alternatively be mineral precipitates produced by inorganic processes. Close comparison of these features with known fossilized bacteria using both SEM and TEM will help determine whether these features are bacteria or inorganic precipitates. Search for chemical biomarkers such as hopanes or lipids is another approach. Even if shown that the Nakhla features are derived from bacteria, they could be formed from bacteria which entered the meteorite during its stay on Earth. While these features are apparently sandwiched between and wrapped in secondary minerals thought to have formed on Mars, detailed isotopic analysis is necessary to positively determine whether the bacteriamorphs and their associated features originated on Mars. Clearly more detailed work is necessary, but the possibility that these features are actually martian bacteria is clearly exciting.

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Fig. 1 (Left) Optical microscope view of crack in Nakhla showing a large number of submicrometer specks. Changing focus shows that specks throughout the depth of the vein in the 30 μ m thin section. (Right) crack filling in Nakhla containing numerous submicrometer specks. The specks are associated with carbonate, clay minerals, and silica-rich glass. Scale bar is 5 micrometers.

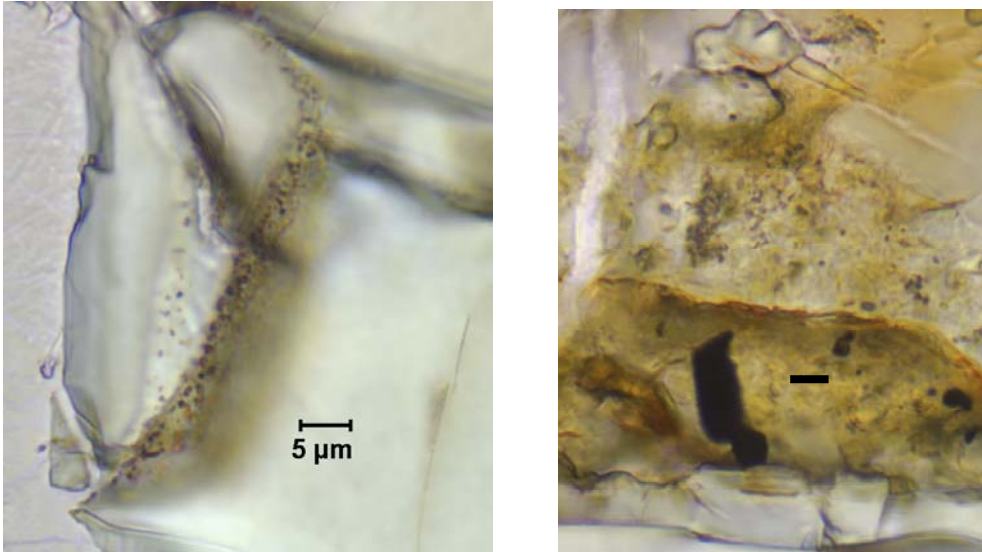
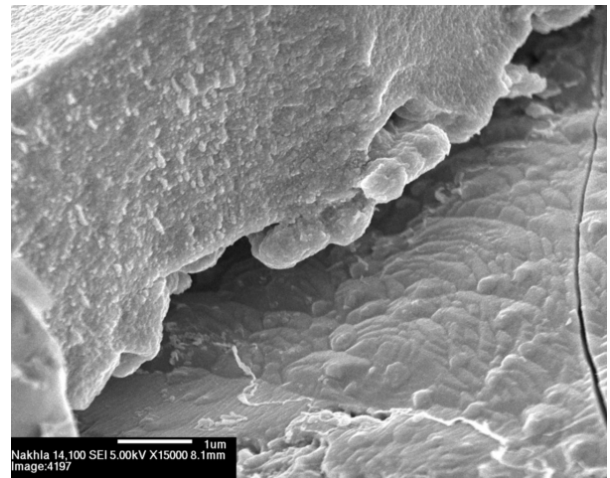
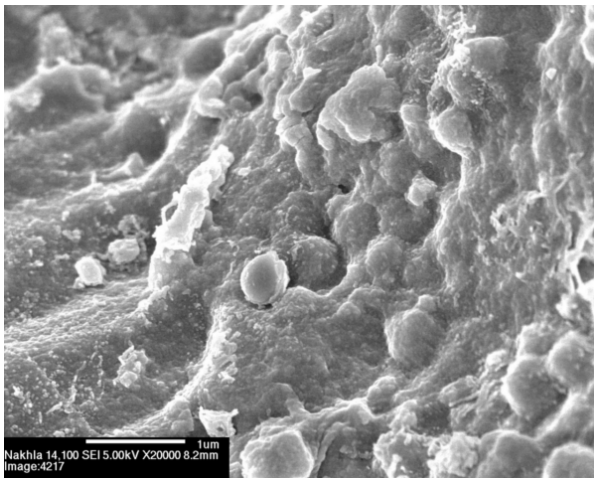


Fig.2. Biomorphs in cracks in Nakhla. (Left) Some of these forms are partly embedded in the matrix, possibly a fossilized biofilm, some are almost entirely embedded, and some appear to be just touching. (Right) The rounded biomorphs are in a crack between a clay layer (top) and a slightly weathered or textured pyroxene surface (bottom).



Volcano-Ice Interactions and the Exploration for Extant Martian Life

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Introduction: Recent discoveries have revealed terrestrial colonies of microbes both in 349 K geothermal groundwater located at a depth of 2800 m [1], beneath glaciers in the Canadian Arctic [2] and subglacial lakes in Antarctica at a depth >3 km [3]. The existence of extremophiles in these subsurface environments has opened up important new directions in the exploration for Martian life. In keeping with NASA's programmatic initiative to "follow the water", exploration for extant life has been focused on the search for zones of subsurface water. Clifford [4,5] identified two environments for liquid water in the region of the Martian North Polar Cap of Mars: melting at the base of ice sheets and magma-ice interactions. The latter idea was also supported by Allen [6] who suggested subglacial volcanic features observed in Iceland (i.e. table mountains and moberg ridges) as possible analogs for Martian landforms observed in some Viking images.

Methods: To further explore glacial and periglacial environments of Mars for sites of recent hydrothermal activity, we conducted a survey of Viking orbiter images for the region north of 70° N. This poster reports preliminary results from that search. Further analysis of recently released Mars Orbiter Camera (MOC) images for several promising sites provided evidence for localized volcano-ice interactions along the margin of the North Polar cap. A detailed morphological comparison of these features with terrestrial analogs is presently underway.

Volcano-Ice Interactions: Icelandic Analogs: Subglacial volcanism, associated jökulhlaup outflow events, and pseudocraters/rootless cones are examples of geothermal-ice interactions observed in Iceland that could also exist on Mars. The Grímsvötn geothermal area located on the Vatnajökull Glacier, boasts a network of active subglacial volcanoes and fissures. The extensive geothermal system that has developed beneath the ice cap is thought to be responsible for repeated jökulhlaup (glacial outflow) events in the Vatnajökull region [7]. In addition, pseudocraters (or "rootless cones") are also present in periglacial areas where lava flows have been extruded over ground ice or shallow aquifers [8]. In such regions, dense fields of small volcanic cones form by phreatic (steam) explosions. The potential for identifying similar geomorphic features on Mars using MOC-scale imaging is great. The following sections provide a brief description of the three types of glacial-magmatic interactions mentioned above and their significance as potential Martian analogs.

Jökulhlaups. A Jökulhlaup is a large outflow event that takes place when a subglacial lake breaks through its containment area along the base of the glacier, bursting through as a voluminous flood. The catalyst for a jökulhlaup is typically a subglacial volcanic eruption that produces progressive filling of a subglacial lake through melting of the overlying ice [7]. Over time, repeated jökulhlaup events create sediment outwash plains. These are common today along the coast of Iceland, adjacent to large ice caps. In the region of Chasma Boreale, Mars, an area previously postulated to have formed by outflows from basal meltwater [4], an analysis of Viking and MOC images shows areas of striated light-over-dark albedo patterns which we interpret to be shallow, braided channel networks that dip downslope, terminating in larger channels. These observations are consistent with the previous outflow interpretations, and the braided channel apron could be the Martian equivalent of an Icelandic outwash plain.

Subglacial Volcanoes. In the Olympia Planitia region of Mars, Viking and MOC images show small, cone-like features on the periphery of the north polar cap, which we interpret to be volcanoes. These features have steep sides and small summit craters, quite unlike the impact craters in the same images. Furthermore the cones do not display the lobate ejecta blankets typical of the rampart craters present there. A localized geothermal hot spot, or perhaps the residual heat of a large impact crater, may have sustained localized volcanic activity along the margin of the ice cap. As with the Grímsvötn volcanic system in Iceland, the eruption of volcanoes beneath glacial ice during a time of a more extensive Martian ice cap, could be expected to produce an active hydrothermal system, which could consequently sustain localized upflows of water from subsurface aquifers.

Pseudocraters. In the same region as the volcanic features described above, Viking and MOC images show a peculiar hummocky terrain along margin of the north polar cap. At MOC resolution, the landforms are comparable to small fields of volcanic pseudocraters (rootless cones) found in Iceland. These features form when hot ash or lava is erupted onto wet or icy ground, generating phreatic explosions. The deposits so formed are sometimes hot enough to sustain local hydrothermal systems during a subsequent cooling phase. Greeley and Fagents [8] have identified similar features at several mid-latitude locations on Mars

Future Work: Currently we are working to integrate MOLA and MOC (meter-scale) topographic data to test our hypotheses about the volcanic origin of the small conical landforms discussed above. Similarly, we will use MOLA data to evaluate the origin of the outwash-like plains adjacent to Chasma Boreale. Combining high resolution topographic and imaging data with rock abundance estimates from thermal inertias acquired by the Thermal Emission Spectrometer (TES) now in orbit at Mars, we hope to more fully assess the origin of these features. These data will also be compared to remote sensing and ground truth data acquired from Icelandic analogs.

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The Organic Content of the Tagish Lake Meteorite

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Carbonaceous chondrites offer a unique record of chemical evolution, the product of presolar and planetary abiotic processes. The Tagish Lake meteorite fell into an icy lake in the Yukon Territory in January 2000 and has an unusual post-impact history in that portions of it were recovered within hours of infall and immediately frozen. With such a collection history, samples from the meteorite may be the most pristine materials of their kind. The organic content of the meteorite has been investigated, and both its insoluble material and extractable compounds were analyzed. ^{13}C NMR spectroscopy shows that the Tagish Lake macromolecular material is dominated by aromatic features and differs from those isolated from both CM (Murchison) and CI (Orgueil) chondrites. Water soluble organics (as amines, carboxylic acids, amino- and hydroxy acids) are present in this meteorite in far lower abundance than in most carbonaceous meteorites studied so far. The only exception, so far, is presented by the suite of dicarboxylic acids, which is quantitatively, if not qualitatively, comparable to those of CM and CI chondrites. Solvent extracts also revealed an unique content dominated by straight chain hydrocarbons and a distinct isotopic composition. Although studies are still in progress, the results of these analyses show the Tagish Lake meteorite has an unusual and surprising organic content, with a distribution that only in part resembles that of CI and CM carbonaceous chondrites.

Detecting Organic Molecules on Mars

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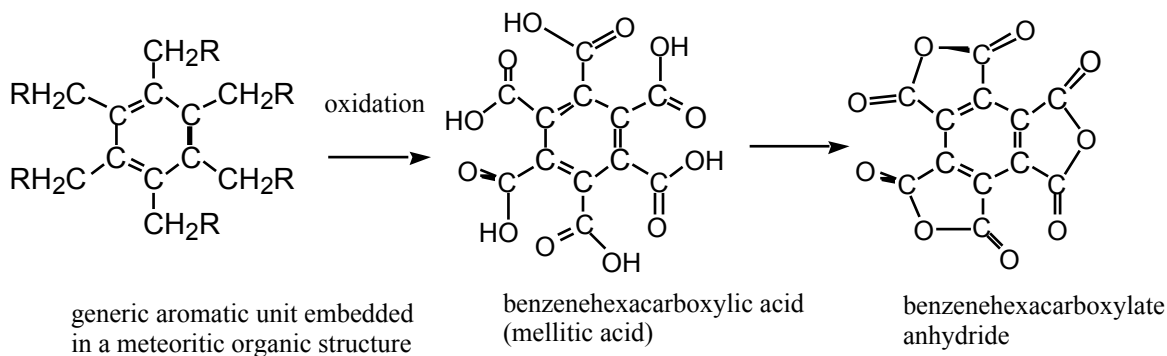
We recently pointed out that substantial amounts of benzenecarboxylic acids should be present on the accessible surface of Mars. This hypothesis was based on an analysis of the intrinsic chemical reactivity of organic molecules that would be delivered to the surface of Mars via meteor. These compounds would not have been detected by the Viking 1976 experiments. Further, if the hypothesis is true, it would greatly alter our view of the "oxidizing" nature of the Martian surface. If these organic compounds are present in abundance, they would serve as a resource on Mars, including as a resource for human habitation.

Almost immediately after the proposal was made, Luanne Becker and her collaborators noted a peak at 288 mass units in the mass spectrum of SNC meteorite. This would correspond to the anhydride of benzenhexacarboxylic acid, predicted to be the principal organic molecule on the surface of Mars.

We have developed a novel approach that converts benzenecarboxylic acids to fluorescent compounds suitable for detection at very low concentrations. This approach is suitable for both Earth-bound research on SNC meteorites (and, in the future, on samples returned from Mars via human effort), and for in situ studies on Mars using the Martian lander.

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Biotechnology Approaches to Life Detection

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The direct detection of organic biomarkers for living or fossil microbes on Mars by an in-situ instrument is a worthy goal for future lander missions. Several new and innovative biotechnology approaches are being explored. Firstly we have proposed an instrument based on immunological reactions to specific antibodies to cause activation of fluorescent stains. Antibodies are raised or acquired to a variety of general and specific substances that might be in Mars soil. These antibodies are then combined with various fluorescent stains and applied to micron sized numbered spots on a small (2-3cm) test plate where they become firmly attached after freeze drying (See Fig 1). Using technology that has been developed for gene mining in DNA technology up to 10,000 tests per square inch can now be applied to a test plate [1,2]. On Mars or the planet / moon of interest, a sample of soil from a trench or drill core is extracted with water and/or an organic solvent and ultrasonication and then applied to the test plate. Any substance, which has an antibody on the test plate, will react with its antibody and activate its fluorescent stain. At the moment a small UV light source will illuminate the test plate, which is observed with a small CCD camera, although other detection systems will be applied. The numbered spots that fluoresce indicate the presence of the tested-for substance, and the intensity indicates relative amounts. Furthermore with up to a thousand test plates available false positives and several variations of antibody can also be screened for. The entire instrument can be quite small and light, on the order of 10 cm in each dimension. A possible choice for light source may be small UV lasers at several wavelengths. Some of the wells or spots can contain simply standard fluorescent stains used to detect live cells, dead cells, DNA, etc. The stains in these spots may be directly activated, with no antibodies being necessary.

The proposed system will look for three classes of biomarkers: those from extant life, such as DNA, those from extinct life such as hopanes, and those from organic compounds not necessarily associated with life such as PAHs, rocket exhaust contamination and other a/pre-biotic chemicals. Both monoclonal and polyclonal antibodies can be used. Monoclonal antibodies react with a very specific compound, but polyclonal antibodies may react to any of a whole family of compounds. Furthermore the technique of phage display to raise antibodies against classically non-antigenic molecules is also being considered [3].

Furthermore technology which would allow a made on earth stamp to be applied is also being investigated. To nullify the possibility of the detection of terrestrial microbial contamination carried on the instrument, we propose to look for generic antibodies to terrestrial microbial cell wall components (several are currently available). Before launch these are applied to the instrument to label any possible contaminating organism with a 'made on earth' stamp. Antibodies against this stamp in the test wells will therefore show a positive reaction upon sampling terrestrial contamination.

One aspect of this proposed experiment is that it must be extensively tested on a variety of terrestrial materials including soils to determine its detection limits, its propensity for false positives, and its ability to discriminate among related compounds. After successful application to both NASA and ESA for the now defunct 2005 mission work is currently underway to choose and evaluate a set of reasonable antibodies and currently we have a list of approximately 60 that we have access to or are immediately commercially available. Extensive laboratory testing of these antibodies will be achieved using the protein chip manufacturing and reading instrumentation at the Carnegie Institute of Washington. This instrument is capable of making protein /antibody arrays on a much bigger scale than is desirable for a flight instrument but it illustrates that the technology is currently available and needs only applying to the specific problem of robotic life detection. The mechanical design of the instrument is underway at Oceaneering Space systems in Houston.

Several key issues must be and are being addressed to ensure success of the concept, these include:

1. Number of steps from initial inoculation to produce a coherent fluorescent signal.
2. Issue of quenching and false positive screening.
3. Tailoring of suitable extraction methods.
4. Detection sensitivity.
5. Survival of reagents in various space simulate conditions.

The unique thing about these problems is for the first time the major hurdles to overcome in a flight instrument have a primarily biotechnological nature. A true extension of Astrobiology and the rationale for Astrobiology missions.

A major objective is to keep the instrument small and simple and to refine sample handling and extraction techniques as well as ascertaining the detection sensitivity of fluorescent and other detection mechanisms.

An important feature of the instrument is its potential for multiple missions. Based on the results of the first mission, the mix of antibodies can be modified, and the instrument can be flown again tailored to zero in on some additional likely compounds. Although this instrument must initially be tailored to a terrestrial organism baseline, so must all initial rationales for life detection. It is only by the application of such specific techniques that we will be able to assess results and modify the search parameters for potentially more exotic metabolisms and biomarkers. Techniques such as phage display may then come

into their own as they can be used to screen for a range of probable mutations / differences in a specific antigen.

Once manufactured the antibodies within these chips can be tailored to a range of applications including automated environmental monitoring for manned missions and sample curation issues, medical screening of Astronauts as well as hand held laboratory instruments for manned missions. Currently our target is to [sic]

A further application of immunological based detection is Chemical Force Microscopy (CFM). In this technique the tip of an Atomic Force Microscope (AFM) is modified using an antibody. As the tip is scanned across the surface of the sample the force at which the tip interacts with the surface can be measured. As the antibody comes into contact with the antigen on the surface the force of the tip / surface interaction (tip retraction) increases. This can be measured and subsequently imaged across the sample surface in 3-D with nanometer resolution [6]. Imaging of Martian meteorites with AFM has already been shown to be viable and useful [7]. This technique will be used to verify MILDI results and to act as quality control in the final antibody chip manufacturing process.

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Application of Computer Tomography for Life Detection

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Perhaps one of the most fundamentally difficult challenges facing those who would search for life is that of scale determination. Spatial scales of life on Earth range over more than 15 orders of magnitude in mass and volume, and more than 8 orders of magnitude in 2 dimensional space. If the distribution of life is sparse in comparison to the background on which it is found, then the choice of the right scale is critical to finding that life. But how does one identify the proper scale? To put this in other words, how does one recognize the “haystacks” in which the needles (biosignatures and evidence of life) might be most profitably searched for? The problem is further exacerbated when conditions get extreme because much of the life moves from the clement surface environment into the pores and more clement environments inside of rocks, minerals and soils. Once encased in their lithic homes, these microbes become nearly impossible to study by standard techniques because of the opacity of the rocks. It is this problem that we propose to address in the work proposed here.

Computer Tomography (CT) has been a very valuable tool in medicine, where the best resolution available has typically been of the order of about 0.5 mm. However, to adapt the approach for life detection of microbial endoliths, the resolution needs to be moved to the micrometer and even submicrometer levels. Thus for the studies proposed here, we begin with a commercially available instrument that can yield resolution of approximately 10 μm . The rational for this is twofold: first, this is the “state of the art” in laboratory instruments; and second, that while the usual size of a microbial cell is about 1 micron, microorganisms tend to live in communities that usually exceed the 10 μm size range. The resolution also depends on the sample size itself, so having a small lab instrument into which small samples can be placed will be beneficial to the resolution.

We have now used several different CT systems, beginning with the medical scanners (Arcadia CT group) for the detection of layered communities in sandstone rocks from Antarctica. Even this crude instrument was able to point to the areas of the rock that were dominated by microbial populations – this provides the critical first information that says, “Go back and look at these sites with other methods.” We showed that without sample preparation or destruction it was possible to gain knowledge as to the presence of density differences suggestive of life.

Dry Mars: Parched Rocks and Fallen Dust

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While “following the water” to find life on Mars, it is easy to overlook evidence that Mars is harshly dry, and to neglect ideas that do not invoke water. Direct evidence for a dry Mars comes from the ALH 84001 meteorite, which has seen little or no liquid water during its last 3.9 billion years on Mars [1]. Its aridity is difficult to reconcile with a Mars of abundant near-surface surface water or with episodes of warm wet climate. Alternative scenarios are also possible, even likely, for the martian gullies and debris flows that have been cited as evidence of liquid water [2]. It is reasonable that the gullies flows are the remnants of massive dust avalanches, comparable to large climax snow avalanches seen on Earth.

ALH 84001. Meteorite ALH 84001 has witnessed the whole span of Martian history, having crystallized from magma ~ 4.5 billion years ago, and departed for Earth at ~ 17 million years ago [3,4]. The carbonate mineral globules in ALH84001 (hosts to purported signs of ancient Martian life [5]) are the only sure signs that the meteorite was touched by Martian water. The globules formed 3.9 billion years ago [6], a time when Mars’ surface is inferred to have been Earth-like. But even the carbonate globules contain nearly no water-bearing minerals (only bits clay, mica, and brucite [7]), which suggests either that the globules were deposited very rapidly (too fast for water and rock to react much) [8], or that the globules were deposited from very saline water [9].

Besides these carbonate globules, the meteorite shows nearly no evidence that it was ever touched by water, either before or after the globules formed [1]. Outside the globules, ALH 84001 contains vanishingly small amounts of water-bearing minerals (clay [10], chlorite, mica, serpentine, gypsum, “rust”) that should form if it had been wet. In fact, the traces of alteration in ALH 84001 could reasonably have been produced during its ~13,000 years in Antarctica [11]. ALH 84001 is less weathered than many meteorites have become in only thousands of years in Antarctica [12]!

The near-absence of weathering or aqueous alteration products in ALH 84001 is a problem for theories of a warm, wet Mars. If ALH 84001’s weathering/alteration history is representative of the whole Martian highlands, then Mars cannot have been wet the way that Earth is. On the other hand, ALH 84001 may represent an unusual sample or state of preservation. In that case, the theories must provide for a protected environment where rock can avoid water for 3.9 billion years.

Dry Gulch. Malin and Edgett [2] present MOC images of debris flows on the steep walls of Martian craters and canyons, most abundant south of 30° S latitude, and tending to be on pole-facing slopes. They inferred that the flows were lubricated by liquid water from

near-surface groundwater aquifers, which could suggest that liquid water (perhaps infested with microbes) is within reach of modest drilling from landed spacecraft. However, landforms similar to those in the MOC images can develop in other ways, including completely dry.

The landforms described in [2] are typical of debris flows or avalanches: arcuate head alcoves or scarps, channels leading downward from the alcove, and a depositional cone or apron at the base. These features do form in debris flows lubricated by water (as [2] suggests), but also form in any setting where a mobilized mass of particles is significantly denser than its environment. Similar landforms can be produced by volcanic ash-flows (lubricated by gases), by submarine turbidity flows (sediment-laden water in clean water) [13], without any fluid at all [14], or by large (climax) snow avalanches [15] (lubricated by air).

To explain the gullies and debris flows, one should look first for mechanisms that are consistent with known geology and processes at the Martian surface. It seems reasonable to suggest that the gullies and debris flows [2] represent large avalanches from thick dust deposits, analogous to climax snow avalanches [15]. Dust is ubiquitous on Mars, is readily moved by wind, forms thick blankets on some slopes, and is known to form small (point) avalanches [16]. To form a large avalanche, the particles must stick together somewhat, and that stickiness could arise from the angularity of the particles [16] or from cementation like that observed at the Viking landing sites [17]. The latitudinal distribution of the gullies and debris flows reflects the abundance of dust in the southern highlands (where Mars' giant dust storms originate). The preference for poleward-facing slopes [2] reflects the wind direction. During major dust storms, in southern summer, surface winds are southward over most of Mars [18].

Conclusion. Mars' surface is now desiccated, and at least part of it has been equally desiccated for the past 3.9 billion years. With this background, and the wealth of atmospheric, imaging, and chemical data available from Mars [19], one must be very cautious in evaluating claims for liquid water recently at or near Mars' surface.

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Concomitant Microbial Carbonate Precipitation and Maskelynite Alteration by *Archaeoglobus fulgidus*

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Introduction: It has been suggested that carbonates in ALH 84001 may have formed approximately 3.95 Ga [1]. The proposed age of the carbonates corresponds to the time period in which microorganisms first appeared and developed on the Earth [2] and conditions on Mars were characterized by abundant water and warm temperatures [3]. $\delta^{18}\text{O}$ isotope values indicate that some of the carbonates in ALH 84001 may have formed at temperatures between 70 and 90° C [4]. Textural observations imply that carbonates in ALH 84001 selectively replaced maskelynite during their formation [5]. These carbonates appear to have an intimate association with maskelynite that is distinct from carbonates associated with orthopyroxene (opx) [6]. We attempted to produce alteration features in opx and maskelynite chips and concomitant carbonate precipitation using the microbe *Archaeoglobus fulgidus*, an archaeon species of ancient origin. Archaeons are believed to be the first types of living organisms to have appeared on the Earth [7]. *A. fulgidus* is a hyperthermophilic, chemolithoheterotrophic archaeon that gains energy through dissimilatory sulfate-reduction and the complete oxidation of lactate to CO_2 [8]. This vent-dwelling, obligate anaerobe grows at an optimum temperature of 83 ° C [8], indicating that it could have potentially thrived under the thermal regime of early Mars.

Methods: Two 50 mg chips of maskelynite obtained from the Manicouagan impact crater (Quebec, Canada) and two 50 mg chips of opx obtained from the Frank ultramafic body (Avery County, NC) were placed in sealed serum bottles containing 50 ml of microbial media (6.5 pH) highly concentrated in Mg^{2+} and Ca^{2+} ions. Bottles were gassed to 2 bars overpressure with a mixture of 20% CO_2 and 80% N_2 in order to create an anaerobic environment. Fifty ml of an *A. fulgidus* culture with a cell concentration of 8.7×10^7 cells/ml were added to two bottles and centrifuged. The supernatant was discarded from the bottles and the remaining microbial pellets were re-suspended in the microbial media present in two of the serum bottles, one containing opx and one containing maskelynite. The two remaining bottles served as sterile controls. All four bottles were incubated at 83 ° C for a period of 4 days. Approximately 1ml of solution was then extracted from each bottle, stained with sybergold and then used to make wet-mount slides, which were analyzed by light microscopy and epifluorescent microscopy. An additional 5 ml of solution were extracted from each bottle and filtered using a 0.022 μm filter. The filters were sputter-coated with carbon and the maskelynite and opx chips from each bottle were

sputter-coated with gold. The filters were analyzed using energy dispersive X-ray (EDX) and the maskelynite and opx pieces were photographed using a Hitachi S-3500N scanning electron microscope (SEM).

Results: Carbonate minerals (Fig. 1A) with ovoid and globular morphologies similar to carbonates associated with maskelynite in ALH 84001 [6] were present on wet mount slides made from bottles containing *A. fulgidus* cells. Cells were located within the interiors of the carbonate minerals (Fig. 1B.) SEM photographs of the maskelynite exposed to *A. fulgidus* cells show extensive rounded and pitted dissolution features (Fig. 2A), carbonates with ovoid morphologies extending out from these alteration features (Figures 2B and 2C) and clumps of *A. fulgidus* encased in biofilm covered with precipitated carbonate (Fig. 2D). None of these features were present in the control samples. EDX data on these minerals indicated the presence of Ca, Mg and Sr. In contrast to the maskelynite samples, opx chips showed no evidence of microbial alteration with simultaneous carbonate precipitation.

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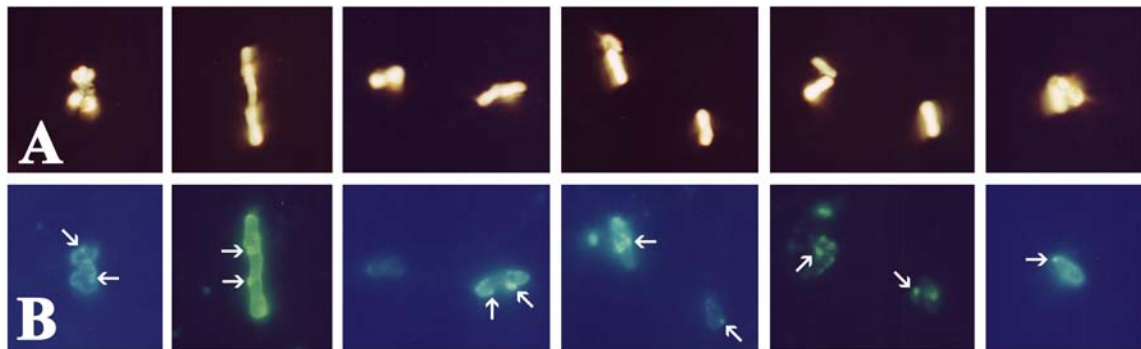


FIGURE 1. Row A shows carbonates 2-3 μm in width and 5-15 μm in length under crossed nicols. Row B shows the same carbonates in row A under UV light. Arrows point to coccoid-shaped *A. fulgidus* cells (green) approximately 0.5-1 μm in diameter.

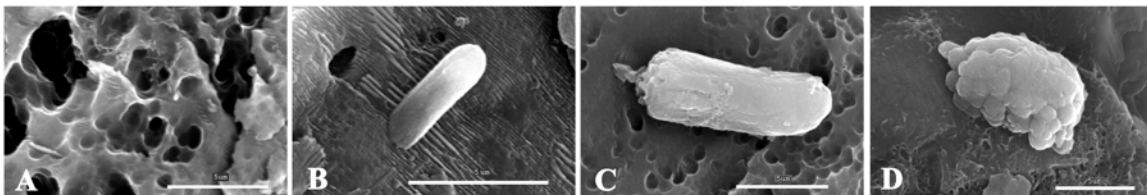


FIGURE 2. 5 μm scale bar. A. Alteration features comprising of rounded dissolution holes. B. & C. Carbonates extending out from alteration features. D. Mineralized cells in biofilm.

Visualization of Microbial Biomarkers by Scanning Electron Microscopy

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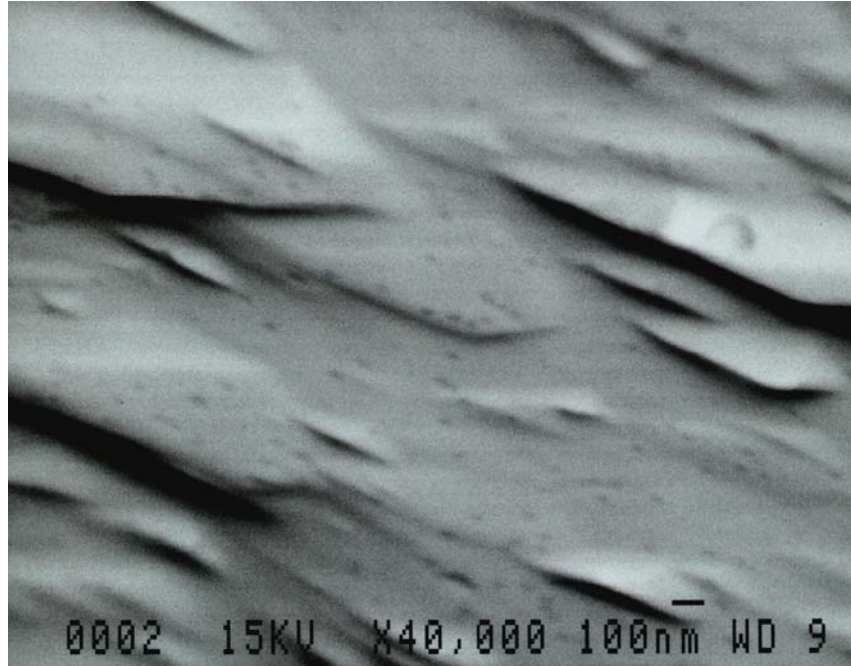
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We are developing tools to link the biochemical structure of selected biomarkers with putative biogenic structures observed in mineralized samples. The detection of evidence of life on Mars and other planets will rely on methods that can discriminate compounds formed exclusively by living organisms. While biogenic compounds, such as amino acids and nucleotides have been discovered in extraterrestrial sources, such as meteorites and comets, their formation can be explained by abiotic means. The formation of cellular structures, or more elaborate organic molecules, such as complex lipids, proteins or nucleic acids, however, is strongly correlated to the presence of even the most primitive life processes. Recent evidence lends support to the hypothesis that life may have once existed on Mars. McKay, *et al.* (1996) describe carbonate globules and ppm concentrations of polycyclic aromatic hydrocarbons (PAHs) in ALH84001, a meteorite originating from Mars ejecta captured by Earth over 13,000 years ago. The localized high concentration of PAHs that follow an increasing gradient from the intact fusion crust towards the interior corresponds to microgram quantities of hydrocarbon. Even though ALH84001 and other similar meteorites have withstood the forces capable of ejecting rock through Mars' escape velocity, upon entering Earth's atmosphere, their core temperatures are likely not to have been raised significantly, as evidenced by the survival of remanent magnetic signatures (Weiss et al., 2000).

Ideal biomarkers of ancient or modern biological life would include molecules that are (or were) pervasive and highly resistant to degradation. Also, requisite methods of detection should be simple, extremely sensitive and broadly inclusive (NASA SP-530). Lipopolysaccharide (LPS), peptidoglycan or pseudopeptidoglycan and beta-glucan are microbial cell wall components which together cover the entire microbial spectrum of eubacteria, archaea and fungi. They are all remarkably resistant to thermal degradation. Fortunately, many antimicrobial defense systems of higher organisms require sensitive detection to combat microbial pathogens. We employ here the primitive immune system of the evolutionarily ancient horseshoe crab, *Limulus polyphemus*. This species relies on

multi-enzyme signal amplification detection of cell wall molecules and they can be applied to the development of useful detectors of life. An extension of this work includes the visualization of microbial signatures by labeling LAL components with chromogenic or electron dense markers. The protein Limulus Anti-LPS Factor (LALF) has an extremely high affinity for LPS (Wainwright, 1990). By coupling LALF binding with colloidal gold labels we demonstrate a correlation of the structures visible by electron microscopy with biochemical evidence of microbial cell wall materials.



Pure silica particles (100 μ) were mixed with cultures of *E. coli* (10^6 cfu/ml). Samples were washed sequentially with buffered saline, LALF, antibody to LALF and finally colloidal gold-labeled Protein A. Negative controls were not exposed to *E. coli* but received identical treatment otherwise. Samples were coated with carbon and imaged on a JEOL JSM-840 scanning electron microscope with LaB₆ source in the back scatter mode with the JEOL annular back scatter detector. 20 nm-scale black spots in this contrast-reversed image originate from electrons back-scattered by gold atoms. Negative controls did not give any signal. Future work will expand application of this technique to soil simulants and mineralized rock samples.

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SNC Meteorites, Organic Matter and a New Look at Viking

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Evaluation of SNC meteorites for indigenous Martian organic material has recently revealed that organic matter is likely present in the planet's crust. If this is true then the results of the Viking GC-MS and their implications for the interpretation of Viking biology experiments may need to be reevaluation. The two Viking landers of 1976 each carried a package of three biology experiments, each designed to detect a different aspect of metabolism that may or may not be present in microorganisms if such life forms exist on the surface of the planet. The instruments consisted of the Pyrolytic Release Experiment (PR), the Gas Exchange Experiment (GEx) and the Labeled Release Experiment (LR) [1]. While the PR and GEx unambiguously obtained negative results with respect to life forms, results the LR were positive based on criteria established before launch [2]. However, largely in light of the failure of a fourth instrument, a mass spectrometer – gas chromatograph (GC-MS), to detect organic matter, the LR responses were later interpreted to have been produced by inorganic chemical oxidants presumed to exist in the Martian regolith [3].

More recently, evidence has begun to grow supporting the possibility that the Viking GC-MS would not have detected certain carboxylate salts that could have been present as metastable oxidation products of high molecular weight organic species [4]. Additionally, despite the instrument's high sensitivity, the possibility had remained that very low levels of organic matter, below the instrument's detection limit, could have been present. In fact, a recent study indicates that the degradation products of several million microorganisms per gram of soil on Mars would not have been detected by the Viking GC-MS. [5]. Since the strength of the GC-MS findings was considered enough to dismiss the biology packet, particularly the LR results, any subsequent evidence suggesting that organic molecules may in fact be present on the Martian surface necessitates a re-evaluation of the Viking LR data. In addition to an advanced mass spectrometer to look for isotopic signatures of biogenic processes, future lander missions will include the ability to detect methane produced by methanogenic bacteria, as well as techniques based on biotechnology. Meanwhile, the identification of Mars samples

already present on Earth in the form of the SNC meteorites [6] has provided us with the ability to study samples of the Martian upper crust a decade or more in advance of any planned sample return missions. While contamination issues are of serious concern, the presence of indigenous organic matter in the form of polycyclic aromatic hydrocarbons has been detected in the Martian meteorites ALH84001 and Nakhla [7, 8, 9], while there is circumstantial evidence for carbonaceous material in Chassigny [10]. The radiochronological ages of these meteorites are 4.5 Ga, 1.3 Ga, and 165 Ma respectively [11] representing a span of time in Earth history from the earliest single-celled organisms to the present day.

Given this perspective on organic material, a biological interpretation to the Viking LR results can no longer be ruled out. In the LR experiment, a solution containing ^{14}C labeled organic compounds was injected into soil samples. The detection of radioactivity in the overhead space would indicate that one or more of the substrates had been chemically converted into a carbon-containing gas. To serve as a control, some samples were heated enough to destroy most known terrestrial microbes so that an indication for life would be a positive response from unheated samples and a negative response from heated samples [12]. On Mars, the LR results had met minimum criteria for a biological interpretation [2] but due to the GC-MS results, the LR responses were later attributed to putative soil inorganic oxidants [3]. Since the time of Viking, studies have been carried out with the objective of determining an oxidant or combination of oxidants that might exist on Mars and have produced the observed kinetics of the LR response. To date, no such agent has been found that produces all aspects of the LR results on Mars [13, 14]. While the above considerations in no way imply the existence of life forms at the two Viking landing sites, inorganic and biological explanations for the Viking LR data should now be considered equally plausible until more complete studies of the Martian surface are carried out. Therefore, in light of the SNC meteorites data and their implications for the possibility of organic matter near or on the Martian surface the Viking biology experiments should thus be seen, not as failures for their inability to provide unambiguous evidence for or against Martian life, but as a foundation for the development of future life-detection instruments.

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Salts in Martian Meteorites: A Complex Martian History

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Rock samples from Mars (i.e., Martian meteorites) contain evidence of low-temperature aqueous weathering that occurred on Mars [e.g., 1, 2]. Weathering features in the Martian meteorites will be of key importance in understanding both the near-surface history of Mars and any possible life (past or present) on Mars. Known Martian weathering features include dissolution textures on primary igneous mineral surfaces, secondary phyllosilicates and oxides, and evaporite minerals (sulfates, halite, and carbonates). Established petrographic criteria [e.g., 2] which identify a secondary phase as Martian include the following: (1) phase present in interior of meteorite but not on exterior (fusion crust); (2) phase included within another, unambiguously Martian, phase (e.g., impact-produced glass); (3) phase partly volatilized; (4) phase terminated by fusion crust; or (5) microfaulting present within phase. We have determined that Martian secondary minerals can also be identified by finding similar weathering features in different Martian meteorites with dissimilar terrestrial histories [3]. For example, the Martian meteorites Nakhla and Shergotty (observed falls in Egypt and India, respectively) contain very similar weathering features and evaporite assemblages, implying that their Martian history is similar.

A characteristic that seems common to Martian meteorite evaporites is that they themselves contain a wide range of alteration features; e.g., the Ca-sulfates in Figs. 1-4. The sulfate in Fig. 1 is fairly fresh but in Fig. 2, the Ca-sulfate is desiccated and partly coated with a later halite deposit. A thin sheet of Martian silicate material (of shock or weathering origin) covers older, fractured Ca-sulfate blades in Fig. 3, clearly demonstrating that the fracturing of the sulfate occurred on Mars. The small Ca-sulfate grain in Fig. 4 is probably the result of a shock event that recrystallized its surrounding carbonate if not the sulfate itself. Halite textures range from massive (Fig. 2) to the distinctive forms in Figs. 5 and 6. The Fig. 5 "stick" is comprised of tiny halite crystals and might have recrystallized from another phase; the associated round patches of tiny crystals may be the result of evaporation from a liquid droplet. It is clear from Fig. 5 that

it is important to determine whether any of the Martian secondary phases originated as different mineral species, as discussed in [4]. The surface texture of the grain in Fig. 6 is very similar to that found on terrestrial aeolian sand grains, suggesting that this form of halite may have been shaped by Martian winds. In summary, the history of the Martian near-surface environment is long and very complex, and factors such as shock or other heating events must be considered in understanding any low-temperature processes, including biological ones, that might have occurred.

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Figure 1: Ca-sulfate (striated material) with little evidence of desiccation/weathering.

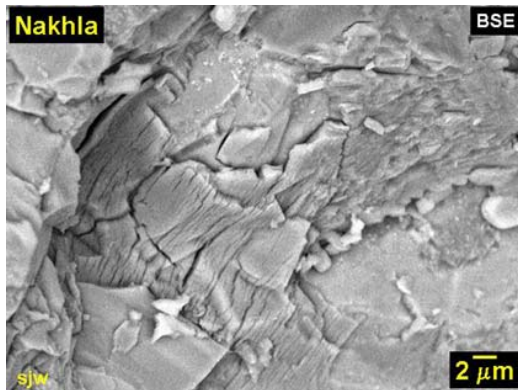


Figure 2: Desiccated Ca-sulfate (bright, striated) partly coated by halite (smooth, medium gray).

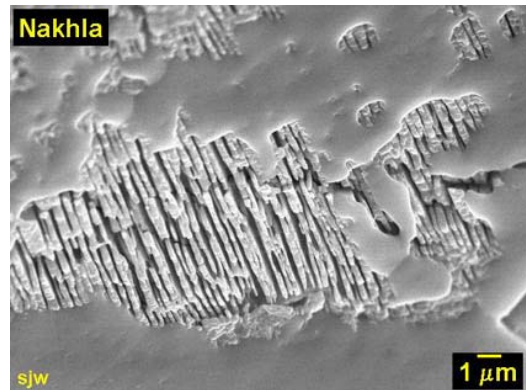


Figure 3: Weathered silicate substrate (bright, patchy areas), overlain by partly eroded Ca-sulfate (blady), in turn coated with thin layer of secondary silicate (medium gray).

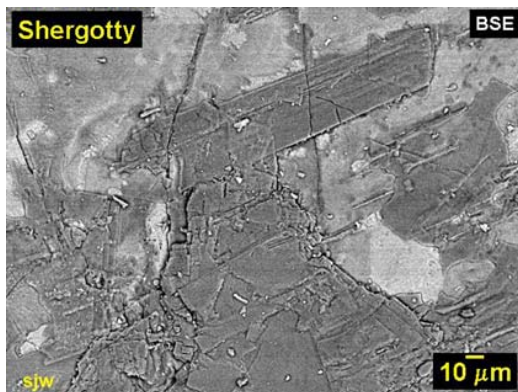


Figure 4: Detrital(?) Ca-sulfate (bright grain at center) included in cluster of Ca-carbonate grains (small crystals). Indications of melting (by impact on Mars or during Earth atmospheric entry) are present.

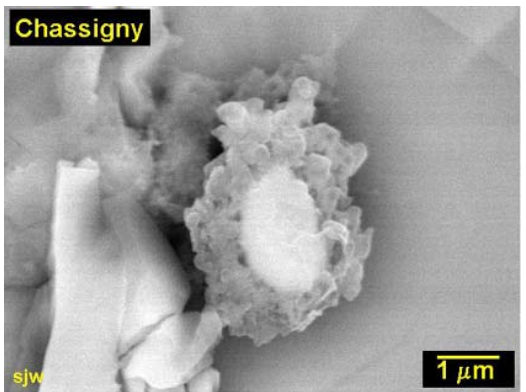


Figure 5: Halite on px substrate; "sticks" made of tiny halite crystals and round halite patches are distinctive of Shergotty.

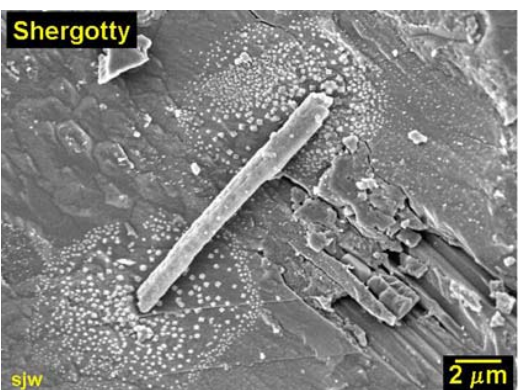


Figure 6: Halite spherule with beveled and pitted surface; this type of halite is scattered in Shergotty; shape may be the result of wind erosion on Mars

